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INTRODUCTION TO
METALLURGICAL CHEMISTRY

INTRODUCTION TO METALLURGICAL CHEMISTRY

FOR TECHNICAL STUDENTS

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PREFACE

THIS little book is intended for the use of technical students who are desirous of making a study of the metals employed for industrial purposes. It must be regarded strictly as a preparatory course, before the study of "metallurgy" proper. Several years' experience in teaching large classes in metallurgy has made it evident that many who are engaged in business during the day, and have, therefore, but little time for study, are unwilling to devote several years to a systematic course of chemistry before commencing the subject in which they are essentially interested. It has been found that two, or in special cases three, evenings a week is the usual limit to the attendance of such students. This permits of only one subject being taken at a time.

The difficulty has been recognised for some years in this school, and at first attempts were made to overcome it by including chemical principles in the ordinary metallurgy classes; but the short time at the disposal of the teachers made the information fragmentary, and of limited value. It was then decided to establish a preparatory class in connection with the metallurgical department, in which chemical principles could be treated *with special reference to the work of that department*; and by careful correlation of this with the other classes, it has been found that the students feel at once that the work

they are doing is directly applicable to their particular branches of industry.

It is becoming more evident every year that the aim in an evening technical school should be rather to increase the general capability of a large number of students than to turn out a few highly-trained men. This end will be best attained by making the subjects taught as self-contained as possible.

The plan of this book is simple. It assumes that those who use it are *practically interested in the common metals*, and that they have no further knowledge of their properties than has been obtained by ordinary observation in a workshop or foundry, so that it is necessary to commence their scientific treatment at the very beginning. The physical properties of the metals and their alloys being fully treated in standard works on metallurgy, more than a passing notice is not devoted to this very important part of the study of metals. Brief references to the more useful properties will be found in different parts of the text. The greater portions of the chapters are taken up with a description of the chemical properties of the common metals, and in the development of chemical principles the metals are made to take as prominent a part as possible. The non-metals are, for the purpose of this book, regarded more as the servants of the metals than as their masters; but this is not from any want of appreciation of their importance, and it is hoped that the common ones are sufficiently described to make them quite familiar. Such of the non-metals as are not of importance in dealing with the chemistry of the metals are either entirely omitted or only briefly noticed, further study being left for a more advanced stage of the subject.

The practical work begins with the study of the effects of air and water on metals. This is followed by a discussion of the

common properties of matter. In dealing with the relation between metals and sulphur the opportunity is taken of introducing the preparation and properties of sulphuric acid. This is followed by a description of the nature and occurrence of common salt and saltpetre, from which, with the aid of sulphuric acid, the other common acids are prepared. By the aid of these compounds common substances of importance in the treatment of metals are prepared and described. Special attention is paid to the reactions between metals and acids; and the chemical equivalents of some metals and non-metals, together with their atomic weights, are considered at some length. The great importance of carbon in the treatment of metals is recognised, and its properties carefully described. This chapter is followed by others in which the important subjects of combustion and reduction are somewhat fully considered. The pronounced part played by silicon and its compounds in metallurgical work is also specially recognised.

Even a superficial examination of the text will show that the book is mainly practical in character, and that the theoretical principles of the subject are developed as far as possible from actual experiments, to be made either by the student in the laboratory, or by the teacher as class demonstrations. Every experiment has been carefully verified, and will give good results, if the instructions are faithfully followed.

It may appear to the systematic chemist that some portions of the subject have been brought into undue prominence, and others either scantily treated or omitted entirely. This is due to the fact that the book does not profess to be a work on pure chemistry, but only an introduction to the chemistry of the metals. It is hoped, however, that nothing of importance has been left out in the development of first principles;

and that the book will be found useful both to teachers and students.

The author's thanks are due to Mr. A. H. Hiorns for reading the proofs, and to Mr. C. R. Clark for executing the drawings.

METALLURGICAL LABORATORY,
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CONTENTS

CHAPTER I

INTRODUCTORY

| | PAGES |
|--|-------|
| Physical properties of bodies—Physical states—Chemical change— Energy | 1-6 |

CHAPTER II

METALS AND OXYGEN

| | |
|---|------|
| The atmosphere—Oxidation of common metals when heated in air —Burning of phosphorus and charcoal—Rusting of iron— Rough determination of the composition of air | 7-20 |
|---|------|

CHAPTER III

METALS AND WATER

| | |
|--|-------|
| Oxidation of common metals by liquid and gaseous water—Decomposition of water by the electric current and by heat—Composition of water by volume | 21-32 |
|--|-------|

CHAPTER IV

PROPERTIES OF MATTER

| | |
|---|-------|
| Definition of matter—Subdivision of matter—Composition of red oxide of mercury—Elements and compounds—Atoms and molecules—Chemical symbols—Law of Avogadro—Metals and non-metals—Classification of common elements—Chemical formulæ and equations | 33-54 |
|---|-------|

CHAPTER V

METALS AND SULPHUR

| | PAGES |
|--|-------|
| Sulphur—Metals and sulphur—Formation of sulphides—Action of heat and air on sulphides—Preparation and properties of sulphuric acid—Determination of formulæ of compounds - | 55-68 |

CHAPTER VI

COMMON ELEMENTS AND COMPOUNDS

| | |
|--|-------|
| Common salt—Hydrochloric acid—Chlorine, bromine, and iodine—Potassium chlorate—Saltpetre—Nitric acid—Ammonium chloride and ammonia—Caustic soda and potash - | 69-84 |
|--|-------|

CHAPTER VII

METALS AND ACIDS

| | |
|---|--------|
| Reactions of common metals and acids—Volume of gas liberated—Metallic compounds formed—Hydrogen—Sulphur dioxide—Oxides of nitrogen—Iron and acids—Alloys and acids—Generation of an electric current by dissolution of zinc in dilute sulphuric acid—Decomposition of metallic salts by an electric current - | 85-115 |
|---|--------|

CHAPTER VIII

CHEMICAL EQUIVALENTS AND ATOMIC WEIGHTS OF
COMMON METALS AND NON-METALS

| | |
|--|---------|
| Determination of equivalents of common metals and non-metals—Vapour density—Atomic heat—Isomorphism—Atomic weights—Valency of elements - | 116-134 |
|--|---------|

CHAPTER IX

OXIDES, ACIDS, AND SALTS

| | |
|---|---------|
| Classification of oxides—Formation of salts—Crystallization of salts—Nomenclature of salts—Chlorides, nitrates, sulphates, carbonates, and other common salts—Basicity of acids - | 135-162 |
|---|---------|

CHAPTER X

CARBON AND ITS COMPOUNDS

PAGES

| | |
|--|---------|
| Occurrence of carbon—Burning of carbon—Composition of carbon dioxide—Native and prepared carbonates—Action of heat on carbonates—Acids and carbonates—Carbonic oxide: its formation and use—Coal—Combustion of coal in open and closed grates—"Air" gas—Coal gas | 163-181 |
|--|---------|

CHAPTER XI

REDUCTION

| | |
|---|---------|
| Action of heat and of heat and reducing agents on metallic oxides and other compounds—Carbon, hydrogen, carbonic oxide, hydrocarbons, metals, and potassium cyanide as reducing agents—Reduction by reaction—The electric current as a reducing agent | 182-199 |
|---|---------|

CHAPTER XII

COMBUSTION

| | |
|--|---------|
| Heat developed by the burning of common combustible bodies—Ignition-point—Zone of combustion—Flame—Luminosity of flame—Transformation of chemical energy into heat during combustion—Measurement of heat | 200-220 |
|--|---------|

CHAPTER XIII

PHOSPHORUS AND ITS COMPOUNDS

| | |
|--|---------|
| Common properties of phosphorus—Extraction of phosphorus—Phosphoric oxide, phosphoric acid, and phosphates—Metals and phosphorus | 221-225 |
|--|---------|

CHAPTER XIV

SILICON AND ITS COMPOUNDS WITH OXYGEN AND METALS

| | |
|---|---------|
| Silicon—Silica—Formation of silicates—Natural and prepared silicates—Fusibility of silicates—Nomenclature of silicates—Fireclay—Glass—Effects of complexity on the fusibility of silicates—General classification | 226-235 |
|---|---------|

CHAPTER XV

WEIGHTS, MEASURES, AND APPARATUS

| | |
|---|---------|
| The Metric System of weights and measures—Measuring apparatus | PAGES |
| —The balance and its use - - - - - | 236-243 |

APPENDIX

| | |
|---|---------|
| Table of elements and atomic weights—Principles used in the correction of the volume of a gas for variations in temperature, pressure, and amount of water vapour - - - - - | 244-247 |
| INDEX - - - - - | 249-252 |

INTRODUCTION TO METALLURGICAL CHEMISTRY

CHAPTER I

INTRODUCTORY

THINGS which appeal to us from outside do so through the agency of our senses. We are thus able to recognise the different objects of the external world which come under our notice, and to distinguish between them by means of those of their properties which affect our sensory organs.

Natural objects are called substances when they are considered with regard to the quality of the material of which they are made, without thinking about its quantity or the position which the objects occupy in space. Thus we speak of water, coal, and lead as substances; but of a *glass* of water, a *lump* of coal, and a *piece* of lead as bodies. In the first case the reference is general, and the quality only of the material is recognised; while in the second case the quantity of the material and its position, as well as its quality, are clearly in mind.

The common and obvious characteristics of bodies by which they are usually recognised belong for the most part to what are called their physical properties. The general appearance of a body and the various changes which may take place in it, without altering the composition of its substance, are due to its physical properties. The term "matter" is used to denote

the substances of bodies generally, and any change in this matter causes a change in the properties of the bodies which contain it.

Physical States of Matter.—The substance of bodies exists in three more or less well-defined physical states—the *solid*, *liquid*, and *gaseous*. A stone affords a good illustration of a solid body, water is the typical liquid, while the atmosphere is the most important gaseous body. Although examples of solids, liquids, and gases are familiar to everyone, it is necessary to consider their general properties sufficiently to be able to distinguish clearly between them.

Solids.—A solid has a definite external form, which it retains as long as it is left to itself. If subjected to pressure in any direction, it resists that pressure without requiring its sides to be supported. A change in form may take place under sufficient pressure, but when the resistance to this change is equal to the pressure which is producing it, the new form is retained or changes but very slowly, as long as the pressure is constant. A hard solid, such as steel, offers great resistance to deformation; but a soft one, such as rubber, changes its form very rapidly under pressure. Both bodies, however, regain their original form on removal of the pressure, if it has not exceeded their power of recovery. The common metals, with the exception of mercury, are well-defined solids.

Liquids.—A liquid must, on the other hand, have lateral support if it is to retain any shape, for it has a tendency to flow to a lower level. The sides of the vessel which contain it supply this support, and thus prevent it from flowing. This tendency to find a lower level causes a liquid to settle down in the containing vessel, and present a definite limiting surface, which is practically flat and horizontal, if the body of liquid is small. With liquids which wet the sides of the vessel the general surface is **raised** a little near the sides; but with liquids which do not wet them a slight **depression** is

observed. These effects are noticed when water and mercury are poured separately into dry test-tubes.

Some apparently solid bodies, such as cobbler's wax, show a decided tendency to flow if left to themselves; and some liquids, such as treacle, are so thick and viscous that they flow very sluggishly. Most of the useful metals, though well-defined solids if left to themselves, may be forced to flow under the hammer, between rolls, or in the press, and so made to take up new forms, which, however, they retain after the operation. A large number of solids, including the metals, may be converted into liquids if made hot enough, and this without any change in their composition.

Gases.—Gases possess the important and distinctive property of indefinite expansion. Thus, if a small body of gas be allowed to enter an empty vessel, it will expand and entirely fill the vessel, irrespective of its size. The gas thins out in the process, and if it expands through a very large space, becomes highly attenuated; its surface is limited only by the sides of the vessel. This is equivalent to saying that if the pressure of the gas were made very small, its volume would become greater than that of any vessel into which it could be put. A gas expands equally in all directions if unrestrained, and so must completely fill any vessel which contains it.

Measurable volumes of gases fulfil, more or less accurately, well-known laws when they are heated and compressed. Also, gases mix together or penetrate each other very readily, which is no doubt due to their property of expansion. Thus a small quantity of an odorous gas liberated in a room will rapidly expand through the air of the room, and may soon be detected in any part of it. It is impossible to keep a gas in an open vessel, for some of the gas escapes and air enters to take its place.

Physical Change.—Many bodies may be made to assume all three physical states in succession, by heating or cooling them. Thus, **water** cooled below its freezing-point becomes

ice, and, if heated continuously at its boiling-point, is converted into **steam**. But the material constitution of the body remains the same; there is no alteration either in the composition or the weight of its substance. All metals can either be melted or converted into vapour at varying temperatures, which in some cases are comparatively low, and in others extremely high.

Chemical Change.—There is, however, another kind of change which bodies undergo when the necessary conditions are observed. It is such as to bring about an alteration in the material constitution of the body or bodies in or between which it takes place. This is called *chemical change*, and is so characteristic as to be easily recognised. It depends upon the chemical properties of the interacting bodies, and requires them to be in very close contact. Even then it is often necessary to start the action by the application of heat. For example, gunpowder may be stored for years without change; but if a light is applied to it the action commences, and the change takes place very rapidly. The interaction of the charcoal, sulphur, and saltpetre, of which the powder is made, results in the formation of a very large volume of gas, which in its expansion produces some of the observed effects.

Energy.—It is such a common experience to see bodies in motion, that we are apt to take the consequent changes in their position as a matter of course, and scarcely give a thought to the cause of the motion. When a man lifts a heavy weight he experiences a sense of muscular effort, to which he ascribes the movement of the weight. The cause of the motion in this case is called muscular **force**. In the same way any change in the position or motion of a body is due to the action of some kind of **force** upon it. The study of the visible motions of bodies forms a branch of mechanics in which the term “force” has a definite meaning, which, however, need not at present be discussed. On the other hand, the parts of a body may be in motion, and this motion

may be increasing or decreasing without any motion of the body as a whole being visible. Thus, when a metal bar is heated it expands, and although this expansion is invisible to the unaided eye it is easily demonstrated by actual measurement. Now, it is evident that the whole body could not expand unless its smallest parts or particles either expand themselves or move wider apart. If it is assumed that the particles move wider apart, the heat which is imparted to the body must be the cause of their increased motion. If then it is necessary that force should be exerted upon a body of sensible size in order to set it in motion, it must also be necessary in the case of a very small body, or particle; the only difference in the two cases is in the relative magnitudes of the forces required.

It follows from this that heat imparted to the metal must exert **force** upon its particles, and so cause them to become wider apart. There is every reason to believe that the ultimate particles of the metal are already in motion, and that the general effect of the additional heat is merely to increase the rate of motion and range of these particles. The cause of the increase may be called **heat force**, but a better name for it is **heat energy**. It must be understood that the motion of the particles of a solid body due to heating it, is of a very restricted character, and the spaces through which they move very small.

When the charge of gunpowder in a cartridge is ignited, the bullet in front of it is caused to move very rapidly, and through a considerable distance. Now the energy which brings about this motion must be stored up in the powder, for it is evident that the mere blow of the hammer on the detonator will not account for the effect produced. Thus, when gunpowder is bought, the effective portion of the purchase is the energy which is stored up in the material of the powder. Further, this energy can be measured by the amount of work it will do when set free. So that it is legitimate to speak about quantity of energy.

As the energy of the exploding gunpowder is developed, the matter of the powder itself undergoes a change in its properties, and new bodies are formed. This is a **chemical change**, and the energy which has been transformed into heat, mechanical work, or other form of energy, was **chemical energy**. It appears to be associated in some way with the bodies between which the change takes place, but it is not evident as long as they remain unchanged. It is, however, possible to measure one form of energy indirectly, while it is being transformed into another form of energy.

In dealing with bodies in general, and the processes going on among them, two things have to be considered ; these are the **matter** of which the bodies are composed, and the **energy** invariably associated with it. It is most probable that the association of the two makes the bodies what they are, and it is certain that any alteration in this relation must cause a change of some kind in the bodies themselves. If during this change no new bodies are formed, it is physical in character, but if new bodies are formed from the old ones, then it is a chemical change.

CHAPTER II

METALS AND OXYGEN

THE atmosphere which surrounds the earth is so essential to life that we become familiar with it at an early age, and unconsciously learn to recognise it by its general properties. Although invisible, it appeals readily to the sense of touch, especially in a high wind. The sensation thus produced is that caused by a substance striking against the exposed parts of the body, and compels us to admit that something material is appealing to us through our senses. If, then, it is admitted that the atmosphere, although invisible, is matter or substance, an investigation of those of its properties which do not appeal to us directly may be commenced. Such work, if methodically carried out, is sure to repay the time and trouble expended upon it.

It will be assumed that the student knows very little about the atmosphere, except that which he has acquired by everyday experience. If the experiments described below, or as many of them as time and the apparatus at command will permit, are carried out, a considerable amount of information about the properties of the bodies under manipulation, and the changes they undergo in the presence of air, will be obtained. As skill in manipulation is only acquired by practice, it is well to bear in mind that an operation, although only partially successful, is sufficiently so if it makes the point it is intended to illustrate clear.

In the following experiments the atmosphere plays as important a part as the other bodies, which are either liquid

or solid, and are therefore under direct observation. The chief aim is to demonstrate the properties of the air, and the behaviour of metals in contact with it.

ACTION OF HEAT AND AIR ON METALS.

Lead.—This metal passes readily from the solid to the liquid state when heated. It has the characteristic properties of the common metals. The sheet lead used by plumbers has a dull appearance, but if the surface is scraped with a knife, it becomes bright, and shows the lustre common to metallic bodies. It is soft, being readily cut with a knife, and can be beaten or rolled into sheets: it possesses the property of malleability in a marked degree. A metal is said to be malleable when it can be hammered or rolled into sheets without cracking at the edges.

EXP. 1.—Test the softness and malleability of a piece of lead by cutting it with a knife, and by hammering it.

The surface of molten lead when exposed to the atmosphere undergoes a gradual change, which is now to be investigated.

EXP. 2.—Cut two squares of glazed paper, about 3 by 3 in., put one in each scale-pan of the balance (Chap. XV.), and make them counterpoise. Roughly weigh about 25 grams* of sheet lead, add to it a scrap of tin,† about 0·25 gram, and weigh the whole accurately. Transfer the lead to an iron pan about 6 inches in diameter

(an ordinary sand-bath pan will do), and place the pan on a circular Bunsen burner, such as that shown in Fig. 1; or on a tripod-stand over an ordinary Bunsen flame. When the lead has melted drop in the tin, and stir well with an iron scraper made of a piece of narrow hoop iron about 15 inches long, and

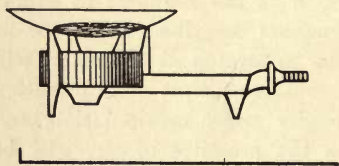


FIG. 1.

bent as shown in Fig. 1. Allow the metal to remain at rest for a

* Grain weights may be used instead of grams: in that case multiply the number of grams by 15·5 to convert into grains.

† The presence of a small quantity of tin as an impurity in the lead increases the rapidity of the action and renders the experiment less tedious than with pure lead. Why it does so need not be considered now.

METALS AND OXYGEN

time, and watch the rapid change in the appearance of its surface. Resume the stirring, and keep the molten metal broken up into globules, so as to expose as large a surface as possible to the air. In from thirty to forty minutes the metal will be converted into a coarse greenish powder, when the pan may be removed and allowed to cool. When cold, transfer the powder with the aid of a small brush to the counterpoised paper upon which the lead was weighed, and weigh it.

| | | |
|---------------------------|-----|--------------|
| EXAMPLE.—Weight of powder | ... | 25·615 grams |
| „ metal | ... | 25·312 „ |
| Increase | ... | 0·303 gram |

This operation is technically known as **drossing**, and if a longer time is taken in carrying it out, a larger increase in weight is obtained. But the experiment may be considered satisfactory if any actual increase in weight is shown, as it is somewhat difficult to remove the whole of the powder from the pan. This is especially the case when some of the dross has softened, through getting too hot, and has stuck to the pan.

EXP. 3.—Transfer the dross obtained in the above experiment to a clean porcelain mortar; add about 10 c.c. of water, and grind up the contents with the pestle; stir well with the finger, and pour off the muddy yellow liquid into a porcelain basin; repeat the operation until the water runs away nearly clear. Allow the basin to stand for a few minutes in order that the suspended solid matter may settle. Then pour off the clear liquid, and carefully dry the residue over gauze or on the sand-bath. When dry, remove the residue from the basin, examine it, and reserve it for future use.

The light yellow powder thus obtained corresponds very nearly to the ordinary massicot (or litharge) in the laboratory bottle. It is usually lighter in colour than the commercial substance, but the longer the drossing stage is continued, the deeper the colour of the product. The washing operation is called levigation, and if the residue from it is examined, it is found to consist of small particles of unchanged lead, which are readily recognised by flattening some of the larger ones on an anvil and scraping them. It is thus evident that at any intermediate stage in the drossing operation the dross consists of the yellow powder and the unchanged metal. As

the action proceeds the proportion of the unchanged lead gets smaller, until finally the whole of the metal is converted into massicot.

EXP. 4.—Put half the massicot obtained from several experiments on one of the pans used for the dressing operation; place the pan on a piece of gauze over a moderate Bunsen flame; stir the powder occasionally, and continue the heating for twelve hours. The whole operation need not be continuous, but the heating may be carried out from time to time as opportunity occurs.

At the end of each heating the colour of the powder is deeper than at the beginning. Finally, it is of a puce colour when hot, and bright red when cold. It will bear comparison with the **red lead** in the laboratory bottle. The operation, which is technically known as **colouring**, should be shared by those students who have contributed massicot to the charge. The pan may be heated over a spare burner, and needs very little attention.

The manufacture of massicot and red lead on the large scale is carried on under similar conditions to the above; but reverberatory furnaces are used, and charges of a ton or more dealt with in one operation.

Copper.—This metal, which has a characteristic red colour, is so very malleable and ductile that it is readily obtained in the form of thin sheet or fine wire. If the end of a thin copper wire is held in the hottest part of the Bunsen flame, it melts. This indicates that the melting-point of the metal is only moderately high.

EXP. 5.—Cut a strip of thin sheet copper, about 1·5 inches wide and 4 inches long, roll it into a loose coil, and weigh it accurately. Put the coil on a clay roasting dish, and place it in a moderately hot muffle. Let it remain there for about half an hour; then take out the dish with the coil on it, and, when cold, reweigh the coil. Note the weight. Put the coil on a piece of smooth paper to prevent loss, and squeeze it with the fingers. The copper has probably all disappeared, and a brittle dark-red mass remains. Grind it to a fine powder in a mortar, and transfer the powder to the dish. Put the dish back into the muffle, and stir the powder from time to time. Leave it in the muffle as long as convenient. When cold,

brush the powder carefully from the dish to the piece of counterpoised paper, and weigh it. The temperature of the muffle should not be above a moderate red heat, or the powder will soften and stick to the dish.

EXAMPLE.—Weight of powder after 2nd heating 3·720 grams
 „ coil „ 1st „ 3·502 „
 „ „ „ 3·000 „
 „ Increase in weight 0·720 gram

A piece of the copper scale, if examined before being powdered, will be found to be blue-black on the outside and dark red inside. It is a mixture of two distinct bodies, one black and the other red, in varying proportions. The proportion of the black body increases with the time of exposure. The powder obtained by crushing the scale is usually dark red in colour, but after further heating it becomes black. On prolonged heating in contact with air the weight of the powder finally becomes constant. A muffle furnace gives the best result but if one is not available the experiment may be made as described below.

EXP. 6.—Bend a strip of sheet copper into the form of a narrow U; weigh it, and suspend it on a piece of clay-pipe stem over a Bunsen flame in such a position as to get the best heating effect when the flame is inside the U. Place a sheet of paper under the burner, and continue the heating for half an hour. Remove the strip, place it on a convenient support, and cover it at once with a dry jar or beaker. When the metal is cold, collect any scale which may have separated from the strip, and reweigh the whole.

EXAMPLE.—Weight of strip after heating ... 10·580 grams
 „ „ before „ ... 10·542 „
 „ Increase 0·038 gram

As soon as the strip begins to cool, the thin scale formed by the action of heat and air upon the metal commences to peel off. This is caused by the rapid contraction of the cooling metal. The change is due to surface action, so that the more finely divided the metal is, the more rapidly it takes place. With the finely-divided metal the maximum increase in weight is obtained in a comparatively short time.

EXP. 7.—Put a gram of finely-divided copper, either fine filings or reduced copper (Chap. XI.), into a weighed porcelain crucible,

and reweigh it. Support the crucible on a pipeclay triangle over a good Bunsen flame. Observe the change which takes place, and continue the heating for fifteen minutes. When the crucible is cold, reweigh it. Grind the residue in a mortar, and examine it.

EXAMPLE.—

| | |
|--|--------------|
| Weight of crucible and copper after heating | 11.900 grams |
| " " " before " ... | 11.647 " |
| Increase | 0.253 gram |

The difference between the black, readily-powdered solid and the metal from which it is formed is very marked.

Tin.—This metal is soft, white, and very malleable. It melts easily, but the change due to the combined action of heat and air takes place slowly at temperatures below a red heat. At a red heat, however, the change is fairly rapid, and is easily effected in a muffle. It is more rapid when impure metal is used. If exposed to too high a temperature, the metal burns and white fumes escape.

EXP. 8.—Weigh carefully 3 grams of tin, with which is included 0.05 gram of lead. Place the metal in a roasting dish, put the dish into the muffle, and keep it at a moderate red heat for an hour. Stir the metal occasionally with an iron scraper, and if it shows signs of burning, draw the dish forward into a cooler part of the muffle. Remove the dish, and, when cold, remove and weigh the residue. Grind up the white powder in a mortar, put it back into the dish, and heat it again for half an hour, with occasional stirring. Weigh again, and note if any increase is obtained.

| | |
|--|-------------|
| EXAMPLE.—Weight of metal after heating ... | 3.793 grams |
| " " before " ... | 3.000 " |
| Increase | 0.793 gram |

Compare the white powder with the metal, and with the "putty" powder in the laboratory bottle.

Iron.—This metal undergoes a somewhat rapid change when heated in the air, and the black scale that collects round an anvil on which red-hot iron is being forged is familiar evidence of this change.

EXP. 9.—Clean a few feet of thin iron wire by rubbing it with emery-cloth, and hammer or roll it into a thin ribbon. Weigh 2 grams of the ribbon, and heat it to a bright red heat on a clay dish in the muffle for half an hour. Allow the dish to cool, grind up the product in a mortar, and, if it is not all reduced to powder,

put the residue back into the muffle, and continue the heating. When the whole has been reduced to powder, weigh it and note the increase in weight.

EXAMPLE.—2 grams of iron increased to 2.766 grams of scale.

The general change which many metals undergo when heated in the air may also take place at the ordinary atmospheric temperature, though *much more slowly*. It is very marked in the case of iron, especially if the air is moist and contains acid vapours. On the other hand, tin will keep a bright surface for a long time under ordinary circumstances, and is used as a coating material for iron to protect it from the rusting action of the atmosphere.

BURNING BODIES AND AIR.

The visible change which takes place when a candle burns is very familiar, for ordinary observation teaches that it disappears during the process, and that light and heat are given out. Further information is easily obtained by simple experiments.

EXP 10.—Fix a short piece of candle in a deflagrating spoon, ignite it, and place it in a large dry bottle, as shown in Fig. 2. At first it burns as brightly in the bottle as in the air outside, but the flame gradually dwindles, and finally disappears. Also, the sides of the bottle are covered with moisture. Now pour a little clear lime-water into another bottle, shake it up, and repeat the burning of the candle in this bottle. When the flame has disappeared, remove the candle and shake the bottle again. The lime-water is turned milky.

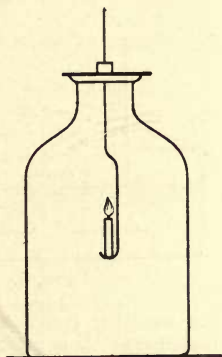


FIG. 2.

Three facts are demonstrated by this experiment: (1) The burning of the candle is dependent upon the presence of air, for if the quantity of air is limited the duration of the burning is limited also; (2) moisture is formed during the burning; (3) the air is so changed by the action that lime-water is turned milky by it.

Exp. 11.—Pour some lime-water into a wide-necked bottle. Place a piece of charcoal on the bowl of the deflagrating spoon, and hold the spoon in the Bunsen flame until the charcoal is red hot. Then put it into the bottle, and allow it to remain there for a minute or two. Remove the spoon, and shake the bottle. The lime-water is turned milky, thus indicating that the burning of charcoal in air produces one of the changes noticed during the burning of a candle in the same body.

The burning of phosphorus and the rusting of iron may be made to give some important information about the nature of the air in which these actions take place.

Phosphorus.—This body is a yellow, waxy-looking solid, which takes fire so readily that it must be kept in water.

Exp. 12.—Fit up the apparatus shown in Fig. 3. A is a glass bell jar of about 2 litres capacity, fitted with a well-greased stopper or a rubber bung. The jar is first graduated by inverting it with the stopper in position, and pouring in 1,200 c.c. of water from a c.c. measure (Chap. XV.). The water-level is marked on the side of the jar, 300 c.c. more water added, and the second level also marked. The jar is then placed over water in the glass trough B, and so supported that the level of the water coincides with the 1,500 c.c. mark when the stopper is out. In this way 1,500 c.c. of air is enclosed in the jar when the stopper is in position, and as the water in the jar forms a movable bottom the air can expand or contract without

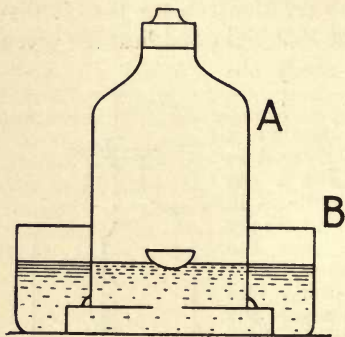


FIG. 3.

gas escaping from or entering the enclosed space. A small porcelain crucible containing a piece of dry phosphorus about the size of a pea is floated on the water inside A. The stopper is removed, the phosphorus touched with the hot end of a piece of wire, and the stopper rapidly replaced. The phosphorus burns, and a dense white vapour fills the jar. In a short time the flame disappears, and the white vapour is dissolved by the water, which gradually rises up the jar to the 1,200 c.c. mark. When the white fumes have disappeared, it is seen that about one-fifth of the original volume of gas has been removed by the burning phosphorus, and that the water has risen in the jar to take its place.

Water is now poured into B until the level of the liquid inside and outside A is the same. This will allow the stopper to be removed without any air entering the jar through the neck, as would be the case if the water-level inside had to fall. The stopper is then removed, and a burning candle lowered into the jar. The flame disappears, thus proving that the residual gas is no longer able to support the combustion of the candle.

As the phosphorus burns, a body is formed which is a white solid at the ordinary temperature. This is easily shown by burning a piece of phosphorus under a dry bell jar standing on a glass plate. As the apparatus cools, a snow-white deposit forms on the glass plate. With suitable apparatus it can be proved that the white solid is heavier than the phosphorus from which it is formed. This increase in weight comes from the air, and Exp. 12 indicates clearly that as the burning progresses the volume of the air concerned in it diminishes, for as the new body is dissolved the water rises in the jar to take the place of that portion of the air which took part in its formation.

Iron.—The rusting of iron takes place slowly under normal circumstances, but if the metal is finely divided and damp, the action is more rapid.

EXP. 13.—Fit up the apparatus shown in Fig. 4. A is a glass cylinder of about 500 c.c. capacity. B is a deep glass or earthenware dish in which A can be inverted and supported above the bottom in any convenient manner. A is divided into five equal parts. To do this, fill the cylinder with water, pour it into a measuring cylinder, and note the volume. Then pour the water back one-fifth at a time, marking the side of the cylinder at the level of each fifth. Cut a strip of filter-paper a little narrower than the internal diameter of A; thoroughly wet the paper, and then rub some fine iron filings on both sides of it. Double the prepared strip, and hang it over a thin wire support placed on C. Invert A over it,

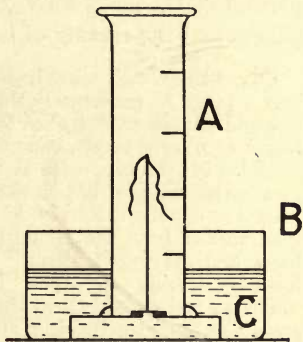


FIG. 4.

and pour water into B until it nearly reaches the first mark on A. Set the whole aside, and, if possible, inspect it from time to time, and note the gradual rise of the water in A. This will go on for a day or two and then cease entirely. If the water rises one-fifth up the cylinder, it shows conclusively that one-fifth of the original volume of air has been removed.

When the action is finished, pour water into B until the level is the same inside and outside A. Raise A a little, and carefully draw out the paper and wire-stand, but be careful to keep the mouth of the cylinder below the surface of the water in B, or air will enter and spoil the experiment. Pass a greased plate under the mouth of A, make it tight, lift out the cylinder with the four-fifths of gas and one-fifth of water in it, and place it mouth upwards on the table. Remove the plate, test the gas with a lighted taper, and quickly replace the plate. Then put the cylinder back into its original position in B, and remove the plate.

When the paper used in the above experiment is examined, the particles of iron on it show distinct signs of rusting. It appears, then, that while the iron is rusting gaseous matter is being absorbed from the air concerned in the action. Also, that the action ceases when about one-fifth of the total volume of the air has been used up. This coincides with the result obtained in Exp. 12, and points to the conclusion that only a portion of the air is active in promoting the burning of phosphorus and the rusting of iron.

EXP. 14.—Weigh roughly 10 grams of red lead, put the powder into a piece of moderately thin-walled combustion-tube, closed at one end and about 6 inches long. Tap the tube until the powder forms a uniform layer about two-thirds up the tube when it is horizontal. Fit the tube with a cork and delivery-tube, and support it in a horizontal position, so that the end of the delivery-tube can be passed under the mouth of A, Fig. 4. (See also Fig. 14.) Heat the tube uniformly in the Bunsen flame by holding the burner in the hand and moving it about. Allow the air driven out by the preliminary heating to escape. Then pass the end of the delivery-tube under A, and strongly heat the red lead until the jar is again full of gas. Continue the heating, and collect a little of the gas in a test-tube which has been filled with water and inverted over water in B.

Remove the test-tube, placing the thumb over its mouth to prevent the escape of gas, raise the thumb, and insert a glowing splint. The wood bursts into flame, and burns much more vigorously than in the air.

Put the greased plate under A, take out the jar, and put it in an

upright position. Place an empty jar by the side of it, and lower a burning candle, first into one and then into the other. The candle is found to burn equally well in the two jars.

Clearly, then, the rusting iron absorbs that part of the air which gives to it the property of supporting the burning of a candle, and the red lead, when heated, gives up a gas which restores this property to the residual air. An examination of the tube shows that the red lead has changed back to the yellow substance from which it was formed. It is evident that the red lead is formed from massicot by the absorption of gas from the air.

Mercury.—There is another experiment which brings out this absorption of a definite gas from the air by the changing metal. But it can only be carried out under exceptional circumstances by the ordinary student, as it requires a moderately high and uniform temperature to be maintained for many hours. The following description will, however, be readily followed, and may be useful for reference later.

Exp. 15.—Fit a 12-ounce glass flask with a good cork, through which is passed a piece of glass tube about 3 feet long and $\frac{1}{4}$ inch bore. Place it securely in a deep sand-bath arranged on a retort-stand, as shown in Fig. 5. Remove the cork, and pour in mercury until the bottom of the flask is well covered. Replace the cork and tube, and put a Bunsen burner under the sand-bath. Heat the bath until the metal begins to boil; lower the flame until the boiling ceases, and then raise and lower it until a little change, either one way or the other, makes the mercury boil or takes it off the boil. Keep the flask at this temperature (about 350°C.) for two or three days. A powder collects slowly on the surface of the mercury, and when removed is found to consist of red scales.

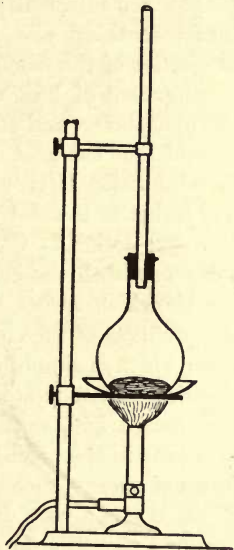


FIG. 5.

If some of this red powder were used in place of the red lead in Exp. 14, a gas with exactly similar properties to that collected from the red lead would be obtained, and liquid mercury would collect on the cool parts of the tube.

Mercury vaporizes rapidly at temperatures near its boiling-point, and the principal use of the long tube shown in Fig. 5 is to act as a condenser, and so prevent the escape of metallic vapour; it also serves for the interchange between the air inside and outside the flask, which is necessary for the continuance of the change.

The Energy of Chemical Change. — The changes brought about during the experiments described in this chapter are sufficiently characteristic to make it quite evident that something else happens besides an alteration in the properties of the reacting bodies. We must take notice of the development of heat which accompanies the disappearance of the phosphorus and carbon during their combustion. It may be said that the heat is due to the energy of combustion, but as combustion is only a particular case of chemical action, it will be better to substitute the more general phrase, "energy of chemical action." Clearly, this energy must be associated in some way with the combustible bodies and with that part of the air which assists in their burning; but it is absent from the products of the combustion. It has been transformed into heat, which is simply another form of energy. The energy of chemical action is stored up in the bodies which take part in the change, and, as the action progresses, is converted largely into heat in the ordinary processes of combustion. But other forms of energy, such as light and electricity, may also appear. There is also a very definite relation between the quantity of heat and any other forms of energy developed, and the quantity of chemical energy transformed. There is very little doubt that no actual loss of energy can possibly take place. As one form disappears, other forms appear in exactly the same proportion. This subject is more fully dealt with in Chap. XII.

SUMMARY.

Several important facts have been demonstrated in the foregoing experiments.

The metals lead, copper, tin, and iron, undergo very characteristic changes when heated in air, and new bodies are formed, which differ in such a marked way from the metals themselves as to suggest complete alteration in their fundamental properties. This is to be recognised as **chemical change**. It must be carefully thought about, and every effort made to understand what it means, as far as the experiments and observations will explain it.

The change in the metals is accompanied by an **increase in weight**, and it is probable that in thinking about this increase the mind will picture to itself the addition to the metals of **something which can be weighed**.

The rusting of iron in a confined volume of air shows that a definite part of the air is absorbed, which is also that part which causes a candle to burn in air. For a candle will not burn in the residual gas. The restoration of this property of supporting combustion to the residual air by the addition of the gas obtained by heating red lead, seems to indicate that the change in the metals—the burning of a candle, charcoal, and phosphorus—are caused by the same substance.

It is a gas, and is called **Oxygen**.

The increase in weight is due to the absorption of oxygen, and the action itself is called **oxidation**. When the action is very rapid, as in the case of burning bodies, it is known as **combustion**.

The residual gas, after removal of oxygen from air, will not support the combustion of ordinary combustible bodies. It is called **Nitrogen**.

However varied the experiments may be, the volume of oxygen absorbed is always found to be about one-fifth the volume of the air acted upon. The composition of pure air is, then, roughly : Oxygen $\frac{1}{5}$ and nitrogen $\frac{4}{5}$ by volume.

Oxygen.—This is the active constituent of the atmosphere, and as such will claim considerable attention later.

Nitrogen.—This gas is inactive, and for our purpose need not be considered further as an isolated body. It will be remembered as a colourless, transparent, odourless gas, which will not allow a candle or other combustible body to burn in it. It reduces the activity of the oxygen of the air by being simply mixed with and diluting it. What was formerly known as pure atmospheric nitrogen is now found to contain a small quantity of a heavier and even more inert gas called *argon*.

The various bodies which have been formed with the co-operation of the oxygen of the air in the foregoing experiments are called oxides; and, as will be proved later, some of them are gases, which, as they form, mix with the residual air. If the actions take place in the open air, as is often the case, the gaseous oxides formed diffuse into the air, and form part of it. As such they may be simply impurities, or they may be essential constituents of a good working atmosphere. This will be considered in future chapters.

QUESTIONS.

1. Describe the changes which take place when lead or copper is heated for some time in contact with air.
2. What do you understand by the term combustible body? Describe an experiment to help your explanation.
3. How would you demonstrate the properties and proportions of the two principal constituents of the air?
4. What is meant by chemical change, and how does it affect bodies between which it takes place?
5. Explain exactly what happens to phosphorus when it burns in air.
6. How is the process of rusting explained? Give an example.

CHAPTER III

METALS AND WATER

Water.—This substance is the typical liquid, and is as important as it is common. It comes next to air as an essential to animal and vegetable life. In the pure state it is a clear, tasteless liquid, which is quite colourless when viewed in bulk. It has the property of dissolving a large number of solids, liquids, and gases more or less readily, and on that account is never found perfectly pure in nature. The natural waters taken in the order of their purity are rain, river, spring, and sea water. The impurities may be removed; therefore all these varieties furnish samples of one well-defined invariable body—**pure water**. Suspended impurities, which make water look dirty, are easily removed by filtering. Dissolved gases are for the most part got rid of by boiling the water. Solids in solution are left as a residue on the complete evaporation of the liquid, and the condensed steam is practically pure water. Liquid impurities are not so readily removed, but by repeated evaporation their complete removal is also possible. The pure water used for particular purposes is known as distilled water, but ordinary drinking water is sufficiently pure for most purposes. It may be convenient to use the substance as ice, water, or steam, but whichever is used the matter is the same. Ice melts or water freezes at a constant temperature, and water boils at another temperature, which is just as constant, if the pressure on its surface is also constant. These are the standard “points” for the ordinary thermometer, and on the Centigrade scale, which is commonly

used for experimental purposes, they are marked 0° C. and 100° C. Further information about the physical properties of water will be found in most works on physics or chemistry.

ACTION OF METALS ON WATER.

Sodium.—This is a soft metal which may be readily cut with a knife. The freshly-cut surface has the ordinary metallic lustre, and somewhat resembles freshly-scraped lead in appearance, but it absorbs oxygen from the air so readily that it tarnishes very rapidly. The metal is usually kept in some liquid, such as mineral naphtha, which is not acted upon by it, so as to exclude the air.

EXP. 16.—Fill a small gas cylinder of about 100 c.c. capacity with water, and invert it over water, as shown in Fig. 6. Be sure that no air is left in the cylinder, or an explosion may occur. Cut a

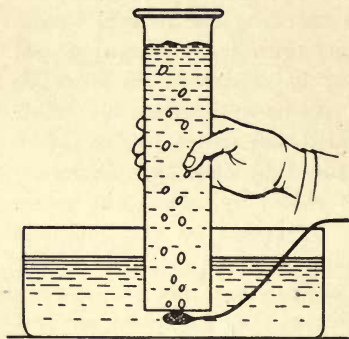


FIG. 6.

piece of sodium about the size of a pea; drop it into the water in the trough, rapidly place over it a gauze spoon, and force it under the mouth of the inverted cylinder. Bubbles of gas escape through the meshes of the gauze, rise in the cylinder, and gradually displace the water. Repeat with similar pieces of the metal until the cylinder is filled with the gas. Sometimes the gas does not get through the gauze readily; in that case tilt the spoon a little, and let the metal escape, when it will rise to the surface of the water in the

cylinder, and there continue its action upon the liquid. Put a greased plate over the mouth of the cylinder, and remove it from the water. Hold the cylinder mouth downwards, remove the plate, and bring a lighted taper near. The gas takes fire, and burns slowly with a yellowish flame.

The visible result of this experiment is that the metal dissolves in the water, and in doing so liberates a combustible gas, which can be collected and burnt.

Magnesium.—This metal is usually sold in the form of ribbon or wire. It has the ordinary metallic lustre, but tarnishes slowly in the air. It is a very light body for a metal, and when heated in the Bunsen flame unites with oxygen so readily as to take fire and burn with a brilliant light, leaving a white residue, which contains magnesium and oxygen.

EXP. 17.—Take a piece of magnesium ribbon, 15 inches long, and make it into a compact coil by wrapping it round a pencil. Draw down a piece of thin $\frac{1}{2}$ -inch combustion-tube in the blowpipe flame, and bend the drawn part as shown in Fig. 7. Push the coil of magnesium into the tube and draw off the other end, bending it the

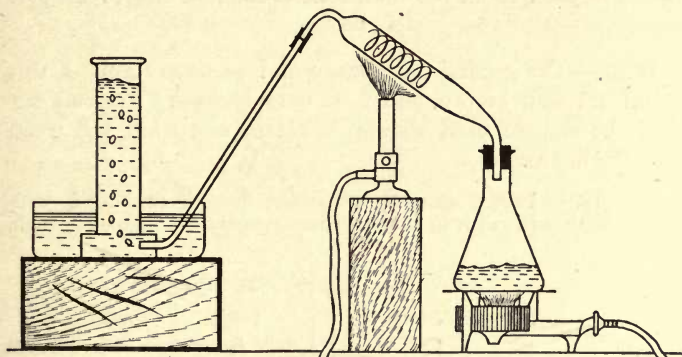


FIG. 7.

same as before, and leaving the body of the tube about 5 inches long. Pass one end through a rubber bung fitted in a small flask containing water, and attach a delivery-tube to the other by a piece of rubber tubing. Arrange the delivery-tube so that it can be directed readily under the mouth of a cylinder of about 200 c.c. capacity, which has been filled, and inverted over water in the pneumatic trough. Boil the water in the flask, and when steam is coming off freely, dry the body of the combustion-tube by carefully moving a Bunsen flame over it. When there is no tendency for water to run back from the upper bend, place the Bunsen flame directly under the metal coil, so as to heat it as strongly as possible. Be ready to insert the open end of the delivery-tube under the mouth of the cylinder directly the metal begins to burn. As the tube is hot from the passage of steam through it, a rubber bung slipped down to the middle saves the fingers in handling it. When

the action has ceased remove the delivery-tube, cover the mouth of the cylinder with a glass plate, and lift it out of the trough. Hold it upside down, remove the plate, and bring a lighted taper to the mouth. The gas burns similarly to that obtained in the last experiment, but the flame is not quite so yellow.

On examination the residue in the combustion-tube is found to be a white powder. It will be useful to compare this powder with that obtained by igniting a piece of magnesium ribbon in the Bunsen flame, and allowing it to burn in the air.

[The apparatus shown in Fig. 7 is all that is necessary, but it will be safer to fix the combustion-tube in a clip to keep it steady.]

Iron.—The general appearance and common forms of this metal are well known, and it is only necessary to point out that the sample used should be clean, and show the usual metallic lustre.

EXP. 18.—Clean a strip of thin sheet iron by rubbing it with emery-cloth, and cut it up into narrow strips about 1 inch by $\frac{1}{16}$ inch.

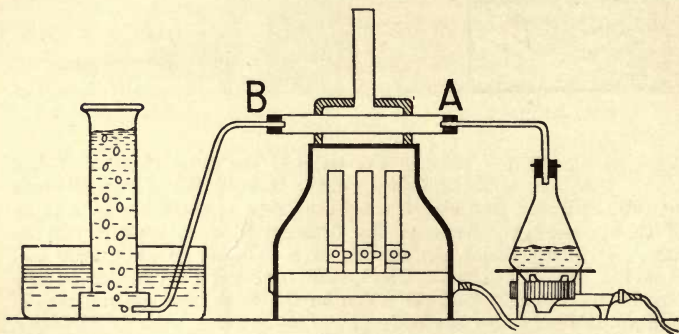


FIG. 8.

Push a plug of asbestos to a convenient position in a thin iron tube about 15 inches long and $\frac{1}{2}$ inch diameter, and put the clean iron through the other end of the tube in sufficient quantity to fill about 6 inches of it. Fit the ends of the tube with rubber bungs and delivery-tubes, and arrange it in a small table furnace, as shown in

Fig. 8. Wrap pads of blotting-paper round the bungs, and keep them saturated with water. This prevents the rubber from becoming overheated. Arrange a small flask for boiling water, so that the steam may be passed directly into the tube. Prepare to collect any gas which may be given off from the other delivery-tube. Heat the iron tube, and boil the water. When the steam comes into contact with the redhot iron, gas is liberated, and collects in the gas cylinder placed to receive it.

Fig. 8 shows the arrangement of the apparatus, and when about one-third of the tube is filled with iron at a good red heat, the gas is liberated rapidly, so that several jars can be easily collected. Closely adhering scale forms on the surface of the iron. The material of the tube also helps the reaction. The most suitable tube for the experiment is the thin, solid-drawn material used for bicycle work. With this, if a furnace is not available, the reaction can be brought about by heating the tube in a good Bunsen flame, but in this case the gas is liberated slowly, and it would be tedious to collect any considerable quantity. By using the foot-bellows and blowpipe a better result is obtained.

Experiments with the Gas.—The first jar of gas may be rejected, as it contains the air which was present in the apparatus at the commencement.

1. Hold a jar of the gas upside down; remove the plate, and bring a lighted taper near to the mouth. The gas takes fire, and burns quietly with a pale-blue flame, and when the burning taper is pushed through the flame into the gas above, it is extinguished, but is rekindled on being pulled back through the flame. The gas itself will burn (combustible), but will not allow a taper to burn in it (non-supporter of combustion).

2. Place a jar with the mouth upwards, remove the plate, and allow it to stand for twenty seconds. Test with a burning taper. The gas has escaped, and the jar is now full of air.

3. Repeat the last experiment, but with the mouth of the

jar held downwards. Very little gas is found to have escaped when a lighted taper is brought to the mouth.

4. Hold an empty jar with the mouth downwards, and bring a jar of the gas into the position shown in Fig. 9.

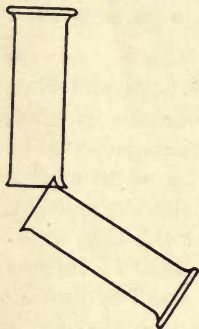


FIG. 9.

Keep them in this position for about half a minute; separate the jars and put plates on them. On examination the lower jar is found to be free of, and the upper one to contain, the greater part of the gas, which now burns with a slight explosion when a lighted taper is put to the mouth of the jar. The last three experiments prove that the gas has a very great tendency to escape in an upward direction from vessels containing it. It is, therefore, a very light gas.

5. Place a jar of air and a jar of the gas mouth to mouth, and allow them to stand, one on top of the other, with the air cylinder at the bottom, for fifteen minutes. See that the ground tops of the cylinders are well greased, so as to prevent any escape of gas. Separate them, and put plates, first on the bottom and then on the top cylinder. Test both with a lighted taper. Equally loud explosions in the two jars show that the mixture of the air and the gas is perfect.

The name of the gas is **Hydrogen**. It burns with a pale blue flame. It will not support the combustion of a taper, or of similar bodies. It is a very light gas, and can be poured upwards. It is colourless, transparent, and odourless when pure; but as collected in the ordinary way it has an odour, due to impurities derived from the materials used in its preparation. The property of gases which enables hydrogen and air to mix together perfectly, although the vessel containing the lighter gas is placed at the top, is known as **diffusion**, and is a common property of all gases. Any number of gases will diffuse into each other, and make a uniform mixture,

providing they do not act upon each other chemically. The composition of a mixture of gases is the same throughout. The heavier gases do not usually separate to the bottom and the lighter to the top, however long the mixture may be kept.

Action of the Electric Current on Water.—The use of the electric current for lighting purposes is now more or less familiar to everyone, and the presence of the white-hot filament in the incandescent lamp is readily noticeable. The heat and light developed in the lamp are due to the resistance offered by the carbon thread joining the terminals of the lamp to the current passing through it. These terminals are connected with copper wires, which are connected in turn with the electric mains through which the principal current is passing, and a small quantity is thus taken off to be used in the lamp. It is an easy matter to cut one of the wires connected directly with the lamp, and to connect the severed ends with a vessel containing water, so that if the current is to pass through the lamp it must also pass through the water. Now it is found that perfectly pure water prevents the passage of the current, and no visible effect upon the liquid is noticed; but if a little acid is added to the water the current passes and the lamp glows. The nature of electricity and the cause of its flow through the wire and the water cannot be discussed at this stage; but it will be sufficient for our present purpose to say that it can be drawn off and used to bring about heat effects and chemical change, just as readily as coal-gas can be passed into a Bunsen burner, and the heat developed by its burning used for a similar purpose.

The apparatus used to contain the water is called a voltmeter, and consists essentially of a glass vessel through the bottom of which two platinum wires, with narrow strips of platinum attached, are fused. These are shown in Fig. 10. The cut ends of the lamp wire are joined to the ends of the platinum wires outside the vessel, and acidulated water is

poured into the vessel to fill in the gap between the two platinum plates. The lamp glows, and bubbles of gas collect on the plates, rise to the surface of the water, and escape into the air. The gas thus liberated can be collected for examination by filling two tubes with water, and inverting them over the plates.



FIG. 10.

EXP. 19.—Fit up the apparatus shown in Fig. 11. This voltameter is a very convenient form of the apparatus. The platinum plates, P and P, are in the tubes A and B, and their wires pass to the outside through the glass. The glass taps at the top of A and B are opened, and water containing a little acid is poured down C until it rises to the level of the taps, which are then closed. The water is now at the same level in the three tubes, and on making the connections with the lamp wires the current passes through the water, and gases are liberated from the platinum plates. The bubbles of gas rise in A and B, and force the water back into C. It is at once noticed that the volumes of the gases collecting in the tubes are not equal, and when sufficient has collected it is seen that the simple relation of 1 to 2 is maintained as long as the action continues. When the level of the water in A nearly reaches the top of the platinum plate, the connection

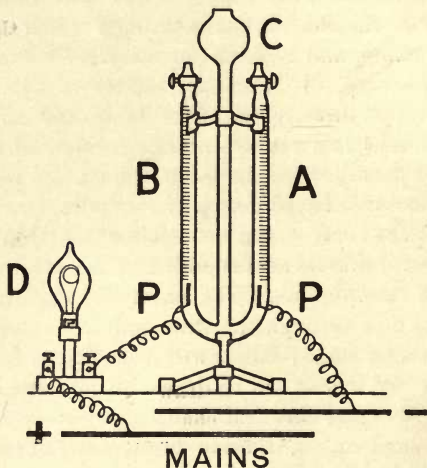


FIG. 11.

is broken, and the liberation of gas ceases. The larger volume of gas is now tested by cautiously opening the tap, and at the same time holding a lighted taper near. The issuing gas, driven out by the fall of the water level in C, takes fire and burns with a pale blue flame. When the gas in B is allowed to escape by opening the tap, and a glowing splint is held near the jet, the wood bursts into flame,

and burns vigorously. These tests are sufficient to indicate the nature of the gases. The larger volume of gas is **hydrogen**, and the smaller one **oxygen**.

If the taps are turned off and the connections reversed, the hydrogen collects in B, and the oxygen in A. This shows that the position of the gases in the apparatus depends upon the direction of the current through the liquid. It is usual to state that the oxygen is liberated on the plate from which the current enters the liquid, and the hydrogen on the plate through which it leaves the liquid. The acid put into the water at the beginning of the experiment is there at the end, unaltered either in quality or quantity. This shows that the gases must come from the water. Thus we have additional evidence that water is a combination of oxygen and hydrogen, and, further, that they are present in the proportion of 1 volume of oxygen to 2 volumes of hydrogen. A simpler form of the apparatus similar to that shown in Fig. 10, in which two tubes, filled with water, are inverted over the platinum plates in the open vessel, may be used. It can be worked readily with two Bunsen cells if the platinum plates are not too far apart.

The two gases can also be collected together, and a very explosive oxy-hydrogen mixture obtained.

EXP. 20.—A is a small bottle containing acidified water, and fitted with a rubber bung, through which pass the two platinum wires tipped with platinum plates, and a delivery-tube leading under the inverted cylinder B. When the current is passed through the water in A, the mixed gases are given off

and collect in B. If, when a small cylinderful has been collected, it is removed and a lighted taper put to the mouth, a loud explosion takes place. The gases combine together again, and water is reformed.

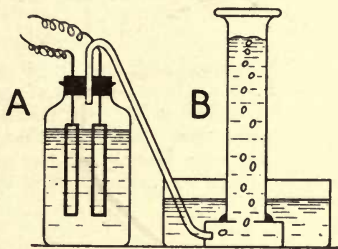


FIG. 12.

If the lighting current is not available for these experi-

ments a voltaic battery of three or four cells may be used. (See Chap. VII.)

Action of Heat on Water.—When steam is raised to a high temperature, it is split up into its constituents, oxygen and hydrogen, but as the temperature falls recombination takes place. If, however, the gases as they are liberated are allowed to mix with some neutral gas, the recombination can be prevented, and evidence of the decomposition obtained.

EXP. 21.—A small long-necked flask, A, is fitted with a bung and delivery-tube. A spiral of thin platinum wire is stretched between

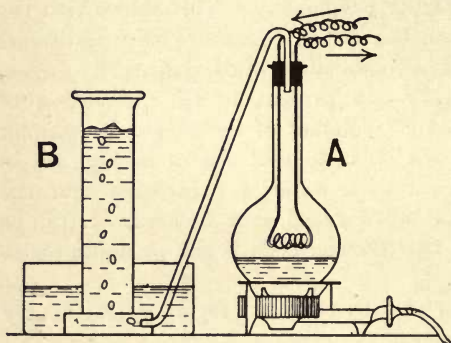


FIG. 13.

the lower ends of two stout copper wires which pass through the bung, and terminate in the middle of the body of the flask. The water in A is kept gently boiling, and the current is sent through the spiral, which is thus raised to a bright red heat by the resistance of the wire to the passage of the current. The steam in direct contact with the

spiral is decomposed, and the liberated gases diffuse into the main body of the steam. Bubbles of gas issue slowly from the delivery-tube, and collect in B. On testing the evolved gas, it is found to be explosive, and to resemble that obtained in Exp. 19. The intense heat of the wire decomposes the water; the current makes the wire hot, but takes no further part in the action.

SUMMARY.

The experiments of this chapter all lead to the conclusion that water is made up of two gases, oxygen and hydrogen. In its decomposition by the electric current the information obtained is very precise, for the water is proved to contain the two gases in the proportion of 2 volumes of hydrogen

to 1 volume of oxygen. Also, when the gases are mixed together in these proportions, and a lighted taper is put into the mixture, recombination takes place with great violence.

Hydrogen has very characteristic properties. It burns with a pale blue flame, and, as will be proved later, water is formed during the combustion. It is a very light gas, being readily poured upwards from one vessel to another. It also diffuses into other gases very readily. The heavier a gas is the more slowly it diffuses. The general law states that the rate of diffusion of gases varies inversely as the square roots of their densities. Hydrogen is the lightest body known, and has, therefore, the highest rate of diffusion.

Ice when heated melts to water; water when boiled is converted into steam; steam when very strongly heated is split up into oxygen and hydrogen. The first two changes are purely physical, for the actual composition of the substance is unchanged. The last is a change in composition, for other forms of matter appear in proportion as the water disappears. This is a chemical change.

The common metals, with a few exceptions, such as sodium and potassium, do not attack pure water at ordinary atmospheric temperatures, and may be left in contact with it for a long time without appreciable change. But this is not the case with natural water, which always contains impurities, and these often act either by themselves, or help to bring about an action between the metal and water. The dissolved oxygen and carbonic acid gases, which are absorbed from the air by water when exposed to it, are active agents in the case of several metals. Thus iron rusts readily, and lead is acted upon somewhat rapidly by such impure water. The presence of solids in solution is also effective in promoting change. This is noticed in the corrosion of those metal portions of ships which are exposed to the action of sea-water. A large proportion of the common metals, when at a red heat, attack water vapour readily, and in all such cases oxides of the

metals are formed. Copper, lead, and tin act very slightly, if at all, even at a bright-red heat.

QUESTIONS.

1. How would you obtain a sample of pure water? Describe its chief physical properties.

2. What kind of body is sodium? State generally what takes place when it is thrown on to water.

3. How may hydrogen gas be obtained in sufficient quantity to test its common properties? Name these properties.

4. Make a sketch of a simple form of voltameter, and explain how you would use it.

5. Can an analogy be drawn between the action of heat and of an electric current upon water?

6. Explain in a simple way the difference between physical and chemical change.

7. Describe the property of diffusion of gases.

8. What is the nature of the bodies formed when metals act upon water vapour?

CHAPTER IV

PROPERTIES OF MATTER

MATTER is the general name given to the stuff or substance of which all bodies are made up. A little thought will make it clear that the total number of different bodies is very large, and it would seem an almost endless task to attempt their classification. Very little difficulty is, however, experienced in arranging the majority of bodies in three great divisions—the *animal*, *vegetable*, and *mineral* kingdoms.

Mass and Density.—It may be stated that the “mass,” or quantity of matter in a body, is a property of the matter which accompanies it without loss or gain through every possible change which the body can undergo. Mass is most easily estimated in practice by weighing, so that the weight of a body may be taken as the measure of the amount of matter in it; but it must be remembered that the terms *weight* and *mass* have somewhat different meanings. The weight of a body, as measured on a spring-balance, *varies* according to the position of the body with regard to the earth, for the pull of the earth upon the body varies with the distance of its centre from the centre of the earth. The force of gravity, which is the cause of the weight of a body, decreases as the distance of the body from the earth’s centre increases, so that a given body would stretch the spring of the balance more at a place near one of the poles than it would at a place nearer the equator, as at the latter the distance of the earth’s centre from it would be greater. Thus, it may be said

that the *mass* of a body depends solely upon the amount of matter in it ; and its *weight* upon the latter, together with the proximity of other bodies to it. But in ordinary weighing on a beam-balance, the body placed in one pan is counterpoised by the weights placed in the other, so that any change in the force of gravity affects the body and the weights equally, and for practical purposes a sufficiently true estimate of the mass of a body is obtained by determining its weight in the usual way.

The *density* of a body is usually stated in terms of the quantity of matter in a unit volume of the body as determined by weighing. But to be accurate, it is necessary to state the temperature of the body in the case of solids and liquids, and both the temperature and the pressure in the case of gases or vapours at the time of weighing. All bodies expand when heated and contract when cooled ; and variations in the pressure to which a body of gas is subjected cause changes in its volume which cannot be neglected even in rough experiments ; but changes in the volume of solids and liquids from the same cause are so small as to be negligible in the ordinary way. Thus the density of gold is 19.3 grams per cubic centimetre at 15° C. ; that of water 1 gram per cubic centimetre at 4° C. ; and that of oxygen 0.00143 gram per cubic centimetre at 0° C. and 76 centimetres barometric pressure. (See Chap. XV. and Appendix.)

The weighing of solids and liquids is a comparatively easy operation ; but in the case of gases it is much more difficult and tedious. In the method of weighing gases adopted by Regnault, two equal glass globes fitted with stopcocks, and having a capacity of several litres, are used. One of the globes is exhausted by means of a good air-pump, and then suspended from a hook fixed to the bottom of the weight pan of a very sensitive balance. This globe serves as a counterpoise for the other one, which is also completely exhausted and similarly suspended from the weighing pan of the balance. The globes are now carefully counterpoised, and the one to

be used for the actual weighing is filled with the pure gas at a pressure slightly greater than that of the atmosphere outside. It is again hung from the scale pan, and the stopcock opened and closed rapidly to bring the gas inside to the same pressure as the air outside. The temperature of the balance case in which the globes hang, and the barometric pressure of the air, are then noted, and the weighing completed. If, then, the capacity of the globe, which determines the volume of the gas, is known, and this volume is reduced by calculation to that which the gas would occupy at the normal temperature and pressure (N.T.P.), the weight of unit volume of the gas under normal conditions is easily calculated. (See Appendix.) Regnault found that :

| | | |
|---------------------------|-------------|------|
| 1 c.c. of hydrogen weighs | 0·0000896 | gram |
| „ oxygen | „ 0·0014304 | „ |
| „ air | „ 0·0012936 | „ |

In the determination of the density of the vapours of solids and liquids which can be vaporized by heat at workable temperatures, it is not necessary to actually weigh the vapours, for the solid or liquid may be weighed and then converted into vapour, and its volume, temperature, and pressure observed. The volume of the known weight of vapour at N.T.P. is then easily calculated, and the density of the vapour obtained. Sometimes it is preferred to weigh the liquid or solid after it has been vaporized and condensed again. The accuracy of these determinations depends upon the fact that no change in the mass of the body takes place during the conversion into vapour.

Conservation of Matter.—All practical experience leads to the belief that, although bodies in general may be made to undergo a variety of changes, the matter in them cannot be destroyed. It preserves its quantity, and passes without loss through every known process to which bodies can be subjected. Nor can matter be created. The changes that take place in bodies which are passing through a given process

may be very complicated, but there is no evidence of gain in the quantity of matter they contain. These statements, that matter can be neither created nor destroyed, refer essentially to its *quantity*, and are supported by every experiment in which the weights of the changing bodies are considered. Any apparent increase in the weight of a body which has undergone change can be traced to the transference of matter to it from some other body that has taken part in the change, and has suffered an equal decrease. This is exemplified in the oxidation of metals in air. The general principle is usually stated under the title of the conservation of matter.

Divisibility of Matter.—It may be taken as an admitted fact that any mineral body can be divided into parts, and that these parts, under exceptional circumstances, may be exceedingly small. All ordinary experience is in favour of this statement, for even the diamond, which is the hardest known body, can be ground to a fine powder on the lapidary's wheel; but it is diamond cut diamond, for diamond dust must be used in the process. But however finely divided a body may be, its ultimate particles must have a definite size, although they may be excessively small. Each particle, however small, must have a definite volume; that is, the mass of matter in it must occupy a finite space to the exclusion of all other matter from that space. This is sometimes expressed by saying that matter possesses volume. Another general experience of all bodies that can be handled is that they possess weight, and that this property is in proportion to the amount of matter in them. If, then, these general properties of matter are admitted, irrespective of the size of the body, the smallest possible particles of a body must occupy a definite volume, and contain a definite quantity of the matter of the body.

Subdivision of Gold.—This metal has many useful properties, and one of the most important is its great malle-

ability. It may be beaten out so thin that a sheet having an area of 50 square inches weighs only 1 grain. A square inch of this gold-leaf is readily cemented to a sheet of glass, cut into 100 strips by a sharp tool, and each of these divided into 100 parts by cutting across the square again at right angles to the first direction. That is, $\frac{1}{50}$ grain of gold may be cut into $100 \times 100 = 10,000$ small pieces, or 1 grain into 500,000 small pieces; and these can be seen with a good pocket lens. But this is not by any means the limit to the subdivision of the gold; for with a special machine it is possible to rule 10,000 lines across the square inch of leaf, and, by ruling again at right angles to the first direction, to cut the whole square into $10,000 \times 10,000 = 100,000,000$ small pieces. Thus a single grain of gold can be mechanically divided up into $100,000,000 \times 50 = 5,000,000,000$ pieces, and these pieces can be seen under a high-power microscope. It may, then, be said that is possible to get a piece of gold which is only $\frac{1}{5000000000}$ grain in weight, and is still visible to the aided eye. This division, extreme though it may appear, is not the limit of possibility, for still finer work can be done.

Dissolution of Common Salt. — Compare the above operation, which depends upon great mechanical skill, with the simple process of dissolving common salt in water. The solid disappears rapidly, and the most powerful microscope fails to detect the particles into which it is divided. That it is simply divided is readily proved. The liquid tastes of the salt, and if the water is evaporated the particles run together again, and the solid salt is recovered. Very little is known about the actual size of the salt particles in the solution, but it is clear that they are smaller than a particle of gold weighing $\frac{1}{5000000000}$ grain. Also, there is evidence in favour of the statement that when a small quantity only of the salt is present in the solution, its separate particles are as small as they can possibly be. As will be explained later,

the term **molecule**, which means a small mass, is used to designate the smallest possible particle of the salt which can have a free existence. The molecules of salt are excessively small, but none the less definite, and go to make up the mass of a lump of salt of sensible size.

Gases.—These bodies are for the most part invisible, but it is certain that the body of any gas is made up of an enormous number of very small particles, or molecules, which are in constant motion. The readiness with which the molecules of gases move about enables them to mix together. The odour of musk, which is due to the escape of particles of the body in the gaseous state, will pervade a whole room, but the finest weighing would probably not detect any difference in the weight of the substance from which the particles had escaped to mingle with the air of the room.

Definite Bodies.—The matter of all bodies is made up of molecules. When the molecules of a body are all alike, it is said to have a definite composition. Such bodies have well-defined properties by which they can be recognised. They may be formed in different ways, but they are always the same in composition. It must not, however, be assumed that every well-known body is of this description; for in many cases further examination brings out the fact that different kinds of molecules are mixed together in the same body. Such bodies are complex in character, and it is part of the chemist's work to separate the molecules of the same kind, and recognise the definite bodies to which they belong. Commercial specimens of definite bodies are seldom perfectly pure, but the adulterating substances are not usually present in sufficient quantity to interfere with their ordinary properties, or with experiments in which they are used.

Red Oxide of Mercury.—This well-known substance has a definite composition. In its common form it is a heavy, red, crystalline powder, which on close examination is found

to be quite homogeneous. Its smallest visible particles are all alike.

EXP. 22.—Weigh 2 grams of red oxide of mercury and introduce it, by means of a gutter of glazed paper, into a piece of combustion-tube closed at one end and about 5 inches long. Fit the open end of the tube with a rubber bung and delivery-tube, and fix the tube in a clip for heating in the Bunsen flame. Pass the end of the delivery-tube under water in a shallow trough, and place over it an inverted gas cylinder of about 100 c.c. capacity, previously filled with water. Heat

the part of the combustion-tube which contains the red oxide in the Bunsen flame until the whole of the powder disappears, or until a very small residue of impurity only is left. The arrangement of the apparatus is shown in Fig. 14.

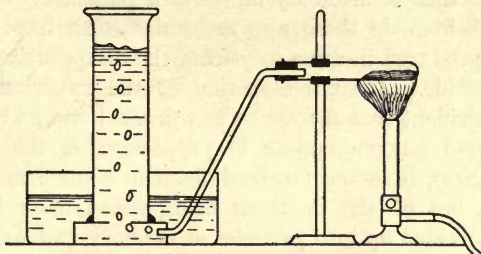


FIG. 14.

When bubbles of gas cease to escape from the end of the delivery-tube, remove it from the water by taking the clip and tubes away bodily. When the combustion-tube is cold, take out the bung and remove the whole of the mercury which has collected on the sides near the open end. If necessary, use a little water to bring away the last particles of metal. A glass rod tipped with a short piece of rubber tube is useful. Dry the mercury by rolling it about in a small tray, made by turning up the edges of a piece of blotting-paper. Weigh the globule of metal.

The difference between the weight of the red oxide and that of the metal obtained from it gives the weight of the gas driven off during the heating. On testing the gas in the cylinder with a glowing splint it is found to be oxygen.

| | | | | |
|--------------------------|-----|-----|-----|-------------|
| EXAMPLE.—Weight of oxide | ... | ... | ... | 2.000 grams |
| „ mercury | ... | ... | ... | 1.846 „ |
| „ oxygen | ... | ... | ... | 0.147 gram |

If a number of such experiments were made, using different weights of the same red oxide, it would be proved on comparison that the relation between the weights of mercury and

oxygen obtained from the oxide is always the same. This is one way of deciding whether a given body has a definite composition or not. It may then be taken for granted that red oxide of mercury is a definite body, and that a weighed quantity of it is made up of an enormous number of exactly similar molecules. The observed effect of heat upon it is very clear. It is split up into two other bodies, which are also as definite in character as the red oxide itself, and each of these bodies is made up of its own particular kind of molecules. Where do these new molecules come from? They must be produced in some way from the disappearing molecules of the oxide. Careful attention to the experiment will make it evident that the action is a gradual one, and that the mercury and oxygen appear in proportion as the oxide disappears. Now, it should not be difficult to picture the individual molecules of the oxide as being acted upon by the heat, and divided up into particles of mercury and oxygen, which then form the molecules of these new bodies. Further, these bodies have both been made the subject of the most exhaustive examination, but no one has yet been able to divide up their molecules so as to obtain molecules of other new bodies from them. Therefore, in the light of present knowledge, the matter of either mercury or oxygen is as simple as it can possibly be.

Clearly, then, definite bodies, of which red oxide of mercury, mercury, and oxygen are examples, belong to two distinct types: (1) Those from which only one kind of matter can be obtained by any known process are called **Elements**; (2) those from which two or more distinct kinds of matter can be obtained are called **Compounds**.

The number of elements is very small compared with the number of compounds formed from them; but the beginner will easily understand the possibility of a very large number of compounds being formed from a small number of elements, if he compares it with that of the formation of the words of a language from the letters of its alphabet.

Matter, then, as we know it, is made up of elements and compounds ; and as the result of a stupendous amount of work, done for the most part during the last 150 years, very definite statements can be made. Some of them are so far-reaching that they are dignified by the name of laws. They will be dealt with in due course. The following definitions will be found useful :

An element is a body from which only one kind of matter can be obtained. A compound contains two or more elements in chemical union. Bodies which do not come within these definitions may be regarded as more or less intimate mixtures of elements or compounds, or of both elements and compounds, as the case may be. They are complex in composition, for their molecules are not all alike. There are numerous examples of such bodies.

Now, it is quite justifiable to inquire whether the molecules of elements are the smallest possible particles of these bodies. Much information has been accumulated in answer to this question. For example, are the particles of mercury and oxygen which leave the red oxide during its decomposition really molecules, or are they still smaller pieces of matter which run together to form the molecules of these elements in the free state ? Some very concise statements can be made at this point, and the beginner may accept them on the understanding that he will gradually become acquainted with the experimental evidence upon which they are based.

Atoms.—The molecule of oxygen is made up of two smaller and exactly similar particles of oxygen called **atoms**. These atoms are indivisible, for in them the extreme limit of subdivision has been reached.

The molecule of mercury when in the gaseous state is not divisible, but is the smallest possible particle of the metal. It corresponds to the atom of oxygen in this respect, and is also called the atom of mercury. So that when the smallest free particle of an element is also the smallest possible particle of

that element, it is called a *one-atom* or *monatomic* molecule. The oxygen molecule is a *more-than-one* atom, or *polyatomic* molecule. These remarks apply to the elements generally.

It is easy to imagine the oxygen (Exp. 22) escaping from the red oxide as atoms, and these atoms running together in pairs to form the molecules of the free gas; and the mercury escaping as atoms, which do not run together, and therefore form molecules by themselves when in the form of vapour. Also, in the oxidation experiments described in Chap. II., the oxygen molecules in the air taking part in the change may be pictured as breaking up into atoms, and joining with atoms of the metals to form molecules of the metallic oxides, which are the products of the change.

It must here be borne in mind that one of the intrinsic properties of matter is its weight, and, however small the particle of matter may be, it must possess this property. Clearly, then, we may speak of the **weight of an atom**.

An atom may be defined as the smallest particle of an element which can exist, or which can take part in the formation of a molecule of an element or compound.

A molecule is the smallest particle of an element or compound which can have a free existence. The masses of all bodies are made up of molecules. The molecules of the vapours of some metals, such as mercury, zinc, and cadmium, are monatomic. As soon as the possibility of the existence of atoms became clear in the minds of the originators of the theory, the want of some method of representing them by signs or symbols was felt. At first these symbols were somewhat fanciful, but now the system has been reduced to a very simple form, in which the symbol representing the atom of an element consists of one or two letters taken either from its common or from its scientific name. Thus the symbol for oxygen is O; for hydrogen, H; for copper, Cu (Cuprum); for lead, Pb (Plumbum). But if O represents the atom of oxygen it also represents its weight; for the weight of an atom is

intimately connected with the atom itself. Very little can be said about the **absolute** weight of an atom, but it is quite possible to compare the different elements with regard to the **relative** weights of their atoms. Hydrogen, which is the lightest body known, has been selected for the standard atomic weight, and the other elements are compared with it. An account of the experimental evidence upon which this rests will be found in Chap. VIII., and tables containing the common elements, with their symbols and atomic weights, are given on pp. 46-7.

The symbolic representation of atoms only requires a little extension to adapt it to the representation of molecules. If it is assumed that both the number and the nature of the atoms in a given molecule are known, no difficulty presents itself; but if the nature only of the atoms in the molecule is known, the best plan is to assume that their number is as small as possible consistent with the composition of the mass of the body.

The molecule of oxygen is said to contain two atoms of the element; it could, therefore, be represented by OO , or by $2O$, but it is generally represented by O_2 , and this combination of symbols is called the formula of the oxygen molecule. The representation of molecules by definite formulæ furnishes a good example of the application of theory to the explanation of the results of experiment, and a short description of the nature of the experimental evidence upon which the molecular formula of oxygen is based will serve a useful purpose in making it clear that formulæ generally depend upon such evidence.

A general statement which is strongly supported by experimental evidence can be made about gaseous bodies. It is known as the **Law of Avogadro**, and is expressed thus :

Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

Thus equal volumes of oxygen and hydrogen contain the

same number of molecules, and double the volume of either gas would contain double the number of molecules. When two volumes of hydrogen are mixed with one volume of oxygen at a temperature above the boiling-point of water, simple mixture takes place, and three volumes of gas are obtained. If the mixture is ignited, the gases combine and steam is formed, which on cooling to the original temperature of the mixture occupies exactly two volumes. Thus the volume of the steam is double that of the oxygen which helps to form it, so that the matter of which the oxygen molecules are composed is distributed into twice as many molecules of steam. That is, each oxygen molecule is divided into two parts during the chemical change by which the hydrogen and oxygen molecules are converted into molecules of water. If, then, the law of Avogadro is true, oxygen molecules must contain at least two atoms of the element, and as no change is known in which they appear to be divided into more than two parts, the inference that oxygen molecules contain two atoms is justified.

The weight of a given volume of any gas compared with the weight of an equal volume of hydrogen, which is taken as the unit weight, is called its density. If, then, it is assumed that a molecule of hydrogen is made up of two atoms, each of unit weight, the molecular weight of the gas is double its atomic weight. By the application of Avogadro's law it follows that the molecular weights of gases are proportional to their densities. So that if the molecular weight of hydrogen is double its density, the molecular weights of other gases are obtained by doubling their densities compared with that of hydrogen. Thus if an element is a gas, or can be converted into gas at a workable temperature, and its atomic weight is known, the number of atoms in its molecule is determined by comparing the weight of a given volume of the gas with that of an equal volume of hydrogen under the same conditions of temperature and pressure. This method of determining molecular weights can be applied to all elements

and compounds obtainable in the gaseous state. The assumption that the molecule of hydrogen contains two atoms is strongly supported by evidence similar to that given above in the case of the oxygen molecule.

Symbols and formulæ are used primarily to represent atoms and molecules, but there is another way of using them which is of great practical importance. It depends upon reasoning such as that which follows :

A given volume of oxygen is made up of an enormous but definite number of molecules, and if n represent this number, the weight of the given volume is represented by $n\text{O}_2$. The atomic weight of oxygen is $\text{O}=16$, and its molecular weight is $\text{O}_2=32$. Now, it is easy to see that n may be such a number that $n\text{O}_2$ represents a definite weight of the gas, say 32 grams ; so that $n\text{O}_2$ might be used to represent a molecular weight of oxygen in grams, or any other standard weights. This is done, but it is usual to omit the n . Thus the formula O_2 is used in two senses : (1) to describe a single molecule of oxygen ; (2) to denote a definite weight of the free gas, as 32 grams 32 pounds, etc. The number 32 always appears in any statement which concerns the weight of a molecule of oxygen, or any number of the same. The symbols and formulæ of bodies in general are used in the same way.

Elements.—These bodies have characteristic physical and chemical properties, by which they can be recognised and distinguished from each other, either by general inspection or by chemical tests. They are divided into two main groups.

Metals.—The larger group contains the metals, several of which are so common, and have such well-defined properties, that everyone is more or less acquainted with them. The metals have two characteristic properties which serve to distinguish them from other elements : (1) The smooth clean surface of a metal has the peculiar appearance known as metallic lustre ; (2) the metals are good conductors of heat and electricity. Most of the common metals are very heavy

bodies, but they vary very much among themselves with regard to this property. Platinum, the heaviest of the common metals, is twenty-five times heavier than potassium, one of the lightest of them.

Non-metals.—The smaller group includes a number of elements whose properties are so opposite to those of the metals that they are known as non-metals. They have no common physical characteristics, but their chemical properties are so marked, that they are taken advantage of in classifying them. This group includes such physically different bodies as sulphur, carbon, and oxygen. A few of the elements occupy the borderline between the well-defined metals and non-metals, and seem to partake of the characters of both. The term *metalloids* is applied to these, but they need not be considered at present.

Some elements occur in such enormous quantities as to be excessively common; others in much smaller quantities, but so widely distributed as to be still common; others again in small quantities, and of limited distribution. These are called rare elements, and, although interesting from the chemist's point of view, are of little known practical value. A list of them is given in the Appendix.

The following tables contain the names, symbols, and atomic weights of the elements which are usually found, either in the free state or as compounds, on the laboratory shelves. Full lists will be found in the Appendix.

COMMON METALS.

| Name. | Symbol. | Atomic Weight. | Name. | Symbol. | Atomic Weight. | Name. | Symbol. | Atomic Weight. |
|-----------|---------|----------------|------------|---------|----------------|-----------|---------|----------------|
| Aluminium | Al | 27·0 | Copper | Cu | 63·0 | Nickel | Ni | 58·5 |
| Antimony | Sb | 120·0 | Gold | Au | 197·0 | Potassium | K | 39·0 |
| Barium | Ba | 137·0 | Iron | Fe | 56·0 | Platinum | Pt | 194·0 |
| Bismuth | Bi | 208·0 | Lead | Pb | 207·0 | Silver | Ag | 108·0 |
| Cadmium | Cd | 112·0 | Magnesium | Mg | 24·0 | Sodium | Na | 23·0 |
| Calcium | Ca | 40·0 | Manganese | Mn | 55·0 | Strontium | Sr | 87·0 |
| Chromium | Cr | 52·5 | Mercury | Hg | 200·0 | Tin | Sn | 118·0 |
| Cobalt | Co | 58·5 | Molybdenum | Mo | 96·0 | Zinc | Zn | 65·0 |

COMMON NON-METALS.

| Name. | Symbol. | Atomic Weight. | Name. | Symbol. | Atomic Weight. | Name. | Symbol. | Atomic Weight. |
|----------|---------|----------------|----------|---------|----------------|------------|---------|----------------|
| Arsenic | As | 75.0 | Fluorine | F | 19.0 | Oxygen | O | 16.0 |
| Boron | B | 11.0 | Hydrogen | H | 1.0 | Phosphorus | P | 31.0 |
| Bromine | Br | 80.0 | Iodine | I | 127.0 | Sulphur | S | 32.0 |
| Carbon | C | 12.0 | Nitrogen | N | 14.0 | Silicon | Si | 28.0 |
| Chlorine | Cl | 35.5 | | | | | | |

Mercury is the only common metal which is liquid at atmospheric temperatures. Arsenic is sometimes classed with the metals, but its chemical properties are more like those of the non-metals. The atomic weights given are only approximate, but they will be found sufficiently accurate for ordinary work.

Compounds.—These bodies are just as definite in their chemical characters and in their constancy of composition as the elements themselves. This cannot be too strongly urged. In fact, the generalizations arrived at as the result of much labour by many men are so all-embracing that they are put forward with much confidence, and are looked upon as thoroughly reliable guides. They are known as the laws of chemical combination. The first one may be stated here, the others will be given later.

The first law of chemical combination is as follows :

A given compound always contains the same elements, and in the same proportions.

Verifications of this law will be constantly presenting themselves, and the student should find no difficulty in finally accepting it. Two examples may now be given. Red oxide of mercury always contains mercury and oxygen in the proportion of 12.5 parts of mercury to 1 part of oxygen by weight. Water always contains oxygen and hydrogen in the proportion of 1 part of oxygen to 2 parts of hydrogen by

volume (see Exp. 19). Or, since oxygen is sixteen times heavier than hydrogen, water contains 8 parts of the former to 1 part of the latter by weight. This will be confirmed later.

Formulae of Compounds.—Now, in Exp. 19 it is proved that 2 grams of red oxide of mercury contains 1.846 grams of mercury and 0.147 gram of oxygen. Assuming that the weight of each element is made up of a definite number of atoms of the element, the ratio between these numbers can be found by dividing each weight by the atomic weight of the element to which it belongs. Thus:

$$\frac{1.846}{200} = 0.0092$$

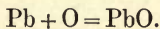
$$\frac{0.147}{16} = 0.0092.$$

The ratio is 1 : 1—that is, the two weights contain the same number of atoms. So that they must leave the oxide molecules in pairs, and are, therefore, present in the molecules in pairs. Clearly, then, the simplest way to represent a molecule of the oxide is to put the symbols together thus— HgO .

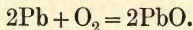
In the decomposition of water by electrolysis it is proved that the constituent gases are liberated in the proportion of 2 volumes of hydrogen to 1 volume of oxygen. Also, by Avogadro's law, the double volume of hydrogen contains twice as many molecules as the single volume of oxygen; and, since all these molecules are *diatomic*, it is probable that the hydrogen and oxygen atoms leave the water molecules in the proportion of 2 : 1. Therefore the simplest way of expressing the water molecule is to write the symbols together thus— H_2O . And there is much evidence in favour of this as the actual composition of a molecule of water. These complex symbols are called *formulae*. Thus, HgO and H_2O are the formulae for red oxide of mercury and water. Next consider Exp. 2. It is not a case of the indifferent absorption of oxygen into lead as a mass, but the individual atoms of oxygen become associated with the individual atoms of lead,

and form molecules of oxide of lead. At any intermediate stage the mass consists of two parts: (a) oxide of lead; (b) unchanged metal. It is either one or the other; there is no intermediate change. In this transformation of lead it is found that 207 parts by weight of lead and 16 parts by weight of oxygen combine to form 223 parts of the oxide. But as these are the atomic weights of the two elements, it appears that the atoms of lead and oxygen run together in pairs to form the molecules of the oxide. Therefore, such a statement as the following may be made:

n atoms of lead ($n\text{Pb}$) and n atoms of oxygen ($n\text{O}$) furnish n molecules of oxide ($n\text{PbO}$). Or, replacing *and* by +, and *furnish* by =, and taking out the n , which is understood, it may be written:

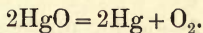


This statement is, as it stands, a chemical equation, and expresses the chemical change under discussion. But, as the oxygen of the air is in the form of molecules, it is usual to write the equation thus:



Here 2PbO means $2[\text{PbO}]$, that is two molecules of the oxide, and the same mode of expressing a number of molecules is always used.

The decomposition of red oxide of mercury is expressed as follows:



And the equation reads thus: 2 molecules of red oxide of mercury furnish 2 molecules of mercury and 1 molecule of oxygen. The beginner will probably have a little difficulty in fully understanding the meaning of symbols, formulæ, and equations, but as he progresses with the practical work, and becomes familiar with them by use, the difficulty will vanish.

Impurities.—Ordinary specimens of elements and com-

pounds usually contain small quantities of other bodies which are regarded as impurities, but these do not as a rule seriously affect the characteristic properties of the bodies under consideration. Almost pure specimens can, however, be obtained if necessary. For example, gold containing less than 1 part of impurity in 10,000 parts of the metal is to be obtained, but it costs about three times as much as ordinary fine gold, which contains about 3 parts of impurity in 1,000 parts of the metal. Zinc and copper containing less than 1 part of impurity in 2,000 parts of the metals are easily obtained, and many compounds are produced in a state of great purity.

Complex Bodies.—These bodies are very numerous and varied. Many of them are common, and have some well-defined properties; but they lack that absolute constancy of composition which is characteristic of elements and compounds. The atmosphere may be taken as an example. Pure mountain air contains at least four substances of definite composition: two elements, oxygen and nitrogen, and two compounds, water vapour and carbon dioxide. The proportion of oxygen to nitrogen is very nearly constant, but the evidence is all in favour of a simple mixture of these gases in air. The proportion of carbon dioxide varies slightly, and that of water vapour considerably, from time to time. Granite is found to contain at least three compounds, which on examination of the polished surface of the stone are seen to be simply mixed together.

Mixtures are often made for practical purposes, and gunpowder, which contains saltpetre, sulphur, and charcoal, is a good example. Such bodies are called **mechanical mixtures**, and when examined under the microscope the various constituents are readily recognised.

The constituents of mixtures can usually be separated from each other without resorting to chemical changes. Such separation can be effected by mechanical means. The removal of particles of iron from brass-dust, and of oxide of

iron from magnetic sands by magnets, are examples. If gunpowder is shaken up with hot water, the saltpetre in it dissolves, and may be completely separated by filtration and washing; the contained sulphur is just as easily dissolved from the dried residue by digesting it with carbon bisulphide; and the charcoal is left as a black residue. On evaporating the solutions of the saltpetre and sulphur respectively, the solids are obtained in the same condition as they were when used to make the original mixture. Complete separation is thus effected without any permanent change in the constituents of the mixture.

Theory of Atoms and Molecules.—In the above statements of facts about matter in general, and in the attempt to explain them, the broad aspects of the atomic theory have been used. The original idea of atoms is by no means a new one, but it was introduced in its modern dress by Dalton, of Manchester, in 1808, who used it most successfully in explaining some facts of chemical combination which he had discovered. Since his time other considerations have necessitated an extension of the original ideas, so as to distinguish between atoms and molecules. It is in this extended sense that Dalton's atomic theory is used by the modern chemist.

When Dalton adopted the idea that matter is made up of small particles (atoms), he assumed that they are all alike in a given body of constant composition. If this is not so, then it should be possible to produce two different specimens of the same compound from its elements by a given chemical change. For if the smallest particles of the elements differ in size in the quantities used, the particles of the compound should differ also. But no such variations in the properties of different specimens of the same compound are known; it is, therefore, a fair inference that the atoms of an element are the exact counterparts of each other. It also follows that if the atoms of elements are alike, the molecules of compounds formed from them must be alike. These assumptions enable

us to account in a simple way for the constancy in the composition of elements and compounds.

It has already been noticed that there are two distinct compounds of copper and oxygen, and it is well known that the weights of copper and oxygen in these compounds are in the proportions of 63 : 8 and 63 : 8×2 , and in no others. It was evidence of this kind, obtained from experiments with some of the compounds of carbon, that led Dalton to the discovery of the law of *chemical combination in multiple proportions*, which may be stated thus :

When one element unites with another element in more than one proportion, the higher proportions are simple multiples of the first proportion.

This law holds rigorously when two elements combine in different proportions to form two or more distinct compounds; and it seems very probable that the molecules of the compounds containing the higher proportions are formed from the molecules of those containing the lower proportion, by the addition of like particles of the other element to them. This was the view that Dalton took, and it enabled him to use the atomic hypothesis in explaining the facts he had discovered.

It is necessary to distinguish clearly between a series of facts and the efforts of the mind to explain them. A theory is a *mind picture*, which keeps our work out of the mechanical rut, and raises it from the region of mere groping to that of intelligent effort. A good theory should not only be able to explain what has happened, but also predict what may happen under certain conditions. And the theory of atoms and molecules has done so much in this direction, that it is accepted with the utmost confidence, and is now regarded almost as a proved truth. The student will, therefore, find good mental training in looking for evidence in its support, and in using it to explain observed facts.

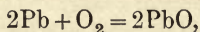
SUMMARY.

Matter is the substance of a body. The term "body" is used to denote a limited quantity of matter which has a definite volume, however great or small it may be. On the other hand, substance is the general term for the matter of a body, without reference to any particular quantity of it. Bodies can be divided into a number of small parts, but there is a limit to their division. Molecules are the smallest possible free particles of matter of any kind. Molecules under certain conditions yield still smaller particles, called atoms, but these cannot have a free existence in the popular sense. The definitions of atom and molecule should be carefully noted, and looseness in their use avoided. They are not interchangeable. An atom is indivisible, and if the smallest free particles of an element are indivisible, they are monatomic molecules as well as atoms. The term "atom" is to be used only in connection with elements, which are bodies containing but one kind of matter. Atoms are the constituent parts of molecules, and the latter are the smallest particles of compounds and of free elements.

There is reason to believe that some compounds are, when in dilute solution, split up or *dissociated* into their elements, the atoms of which are more or less free. These are the *wandering atoms* or *ions* of the electro-metallurgist. Also it is possible to obtain some elements in a simpler state of division than that in which they exist in the ordinary way, by exposing them to a very high temperature. But in both cases the atoms come together again when the separating cause is removed. Atoms are represented by symbols, molecules by formulæ. To indicate the number of similar molecules, a figure is written in front of the formula of the molecule, as 2H_2 , 3PbO .

A chemical equation is the same as any other equation, with respect to the equality of its two sides. But this equality refers only to the number and quality of the atoms on the

two sides, which must be the same, however varied their redistribution in the molecules may have been. Thus in the equation



there are two atoms of lead and two atoms of oxygen on both sides, but the atoms of the molecules of the elements on the one side have been redistributed into molecules of oxide of lead on the other.

A theory should always be accepted with an open mind, and judged according to its ability to explain observed facts. If it does this satisfactorily, as is the case with the atomic theory, it may be used freely.

NOTE.—The investigation of radio-active bodies, which received such an impetus by the discovery of radium, seems to point to the slow breaking down of atoms into still smaller particles. This can, however, be only casually referred to in an elementary work until the nature of these particles is better understood, and its influence upon our present idea of atoms more settled.

QUESTIONS.

1. Give a definition of matter. Give examples of the division of bodies into small particles.
2. What is a definite body? Illustrate your answer by reference to water.
3. Describe an experiment in which decomposition into simpler forms of matter takes place.
4. Define the terms atom, molecule, element, compound.
5. How may symbols be used to represent the proportions of the elements in a compound?
6. What do you understand by the terms "hypothesis" and "theory"?
7. Find the formulæ of the oxides of iron and copper, having given that 4 grams of iron combine with 1.714 of oxygen, and 6 grams of copper with 1.52 of oxygen.

CHAPTER V

METALS AND SULPHUR

Sulphur.—This well-known element is found associated with earthy matter in volcanic districts. It is present in the elementary state, and is called native sulphur. The crude material is carefully heated, which causes the sulphur to melt and drain away, leaving the greater part of the earthy matter behind. The substance thus obtained is still impure, and is known as crude sulphur. To complete the purification the crude material is put into a retort and strongly heated, when the sulphur is converted into vapour. This passes through an opening in the retort into a cooling chamber, where it condenses to the liquid state. The hot liquid collects in the bottom of the chamber, from which it is allowed to run into wooden moulds, and cast into cylindrical sticks. This variety is called **roll sulphur**. If the chamber into which the vapour passes is sufficiently cool the condensed material takes the form of a fine powder, which is called **flowers of sulphur**. These are the common forms of commercial sulphur, and also of the purest.

A considerable quantity of sulphur is also obtained as a by-product in certain chemical and metallurgical operations, so that we are not entirely dependent upon the native form of the element.

Action of Heat on Sulphur.—Roll sulphur is a pale yellow, brittle, crystalline solid, which, when heated, melts to a clear amber-coloured liquid at 114.5°C . On continuing the heating, the liquid gets much darker in colour, and between

220° and 250° C. is thick or viscous like treacle ; above the latter temperature it becomes thin again, but is still dark-coloured ; at 448° C. it boils, giving off a dark-red vapour. On cooling, the vapour condenses to the liquid again, which then passes through similar changes to the above, but in the inverse order, and so returns to the solid state. If, when in the thick condition, the liquid is poured into cold water, a soft solid mass, called **plastic sulphur**, is obtained.

EXP. 23.—Break up some roll sulphur into small pieces, and half fill a test-tube with it. Heat the tube in the Bunsen flame, and observe the changes which take place up to the boiling-point. Allow the tube to cool, and when the liquid gets thick pour the greater part of it into cold water. Note the change in colour of the remaining liquid, and when it is amber-coloured pour some into water. The residue solidifies on the side of the tube. Examine the water-cooled portions : the one is a stringy, plastic mass ; the other consists of hard, brittle lumps.

It may be inferred that to get sulphur into the plastic form its temperature must be raised above 220° C. before it is suddenly cooled. Also that some change in the molecules themselves, or in their relation to each other, must take place about that temperature, and that the sudden cooling prevents the reversal of this change. The plastic mass passes slowly back to the hard yellow form at ordinary temperatures, and more rapidly at 100° C.

EXP. 24.—Melt about $\frac{1}{2}$ pound of sulphur in a large clay crucible, and allow it to cool slowly until a crust forms on the surface. Break the crust, and pour the remaining liquid into a dish of water. The sides and bottom of the crucible are found to be covered with a mass of long, transparent, needle-shaped crystals.

EXP. 25.—Put about a gram of powdered sulphur into a test-tube, and add to it about 5 c.c. of carbon bisulphide. Shake the tube until most of the sulphur is dissolved ; then pour the clear liquid into a small evaporating basin, nearly cover the basin with a clock glass, and put it in a fume chamber to evaporate. When some well-defined crystals have formed, pour off the remaining liquid, and remove them for inspection.

On looking at the crystals with a strong magnifying-glass or under a microscope of low power, some well-formed speci-

mens will be observed. They are generally of two shapes, similar to *a*, *b* (Fig. 15), but the first shape usually predominates. They both belong to the rhombic system.

The experiments described above reveal three distinct forms of sulphur.

1. Octahedral crystals belonging to the rhombic system, which is the stable form found in native sulphur, roll sulphur, etc.

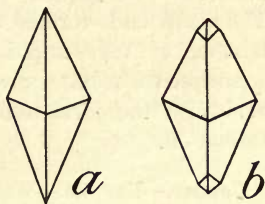


FIG. 15.

2. Needle- or prism-shaped crystals belonging to the monoclinic system, which gradually pass back to the stable form, with evolution of heat. Melting-point 120° C.

3. The plastic form, which is insoluble in carbon bisulphide, and gradually passes back to the stable form, with evolution of heat.

These are **allotropic modifications** of sulphur. This subject will be referred to again in a later chapter, but for fuller details of the varieties of sulphur a larger work must be consulted.

Action of Heat and Air on Sulphur.—When any form of sulphur is heated in air it melts, and then takes fire, burning with a pale blue flame. Oxygen from the air unites with the sulphur to form a colourless transparent gas, having a powerful odour, which is usually described as the smell of burning sulphur. It dissolves readily in water, and the solution smells of the gas, which is a product of the oxidation of sulphur, and is, therefore, an oxide. It is proved by experiment to contain equal weights of sulphur and oxygen. The atomic weights of its elements are $S=32$ and $O=16$, so that its simplest formula is SO_2 . This is also the true molecular formula of the gas, as indicated by its vapour density.

Metals and Sulphur.—When the common metals are

heated with sulphur a very marked change takes place, which is as well defined as that brought about between the same metals and the oxygen of the air under the influence of heat. The compounds formed are metallic sulphides, and include a number of very important metalliferous bodies. Accurate quantitative results are easily obtained, so that experiments on the formation of sulphides give much useful information.

Copper.—EXP. 26.—Weigh accurately 2 grams of finely-divided copper, either in the form of filings or of the reduced metal. Transfer it to a clean dry test-tube by means of a paper gutter. Weigh roughly 1 gram of powdered sulphur, and add it to the copper, well mixing the two by carefully shaking the tube. Heat the end of the tube in the Bunsen flame until the action commences, and when it has ceased return the tube to the flame, and heat it strongly until the excess of sulphur is driven well up the tube. Allow the tube to cool in a slanting position, so as to prevent any liquid sulphur from running back on to the solid residue. Invert the cold tube over a piece of glazed paper, and let the bluish black residue fall out. Weigh this residue. Grind it up in a mortar, and look at the powder under a good magnifying-glass. There is no trace of either free copper or sulphur to be seen; the body appears to be perfectly homogeneous. Mix a little copper and sulphur together; look at the mixture under the glass; put it into a test-tube with a little water, and well shake the tube. The copper settles to the bottom, and the sulphur is suspended in the water. No such separation can be brought about with the residue after the mixture has been heated.

| | | | |
|----------------------------|-----|-----|-------------|
| EXAMPLE.—Weight of residue | ... | ... | 2.507 grams |
| „ copper | ... | ... | 2.000 „ |
| „ sulphur | ... | ... | 0.507 gram |

That is, 2 grams of copper combine with 0.507 gram of sulphur to form 2.507 grams of copper sulphide.

The weight of the sulphur absorbed by the copper is obtained by difference, but this is perfectly legitimate, for practically no copper escapes under the conditions of the experiment; it is, therefore, quite clear that the increase in weight is due to the absorption of sulphur by the metal.

This definite body with its constant composition is copper sulphide.

Now, bearing in mind the idea that the actual weight of each element in the sulphide is made up of a large number of atoms, and that the relative weights of these atoms are $\text{Cu} = 63$, and $\text{S} = 32$, it is easy to understand that, by dividing the actual weights by the relative weights, the ratio between the numbers of the atoms of copper and sulphur combining to form the molecules of sulphide is obtained. Thus :

$$\frac{2}{63} = 0.032 \text{ and } \frac{0.507}{32} = 0.016.$$

The ratio is evidently 2 : 1, and the simplest formula for the compound is Cu_2S .

Iron.—EXP. 27.—Repeat the last experiment, using 2 grams of fine iron filings and 1.5 grams of sulphur. After heating, the residue sticks to the sides somewhat, and it is necessary to break the tube and remove the pieces of glass from the residue before weighing it.

| | | | |
|----------------------------|-----|-----|----------------|
| EXAMPLE.—Weight of residue | ... | ... | 3.145 grams |
| „ iron | ... | ... | 2.000 „ |
| „ sulphur | ... | ... | <u>1.145</u> „ |

That is, 2 grams of iron combine with 1.145 grams of sulphur to form 3.145 grams of iron sulphide.

A magnet will remove the iron from the mixture of iron and sulphur before it is heated ; but no such separation is possible after the reaction has taken place. The definite compound iron sulphide is formed.

It should be borne in mind that the metal and sulphur can be mixed together in any proportions, and easily separated again ; but neither variation in proportions nor easy separation is possible when the elements are united in the sulphide. Thus a clear distinction can be drawn between a mixture of two elements, and a *compound* of the same. Read the statement of the law on p. 47.

Taking the atomic weights $\text{Fe} = 56$ and $\text{S} = 32$, and using

compounds prepared as above are usually described as artificial sulphides, to distinguish them from the naturally occurring ones.

Natural Sulphides.—The majority of the common metals are found in the earth's crust as sulphides mixed with earthy matter, and when the metals they contain can be profitably extracted from them they form the useful ores of these metals. Thus, **Galena** contains lead sulphide, PbS . **Copper Pyrites** contains copper and iron sulphides, Cu_2S , Fe_2S_3 , and is used as an ore of copper. **Iron Pyrites** is almost entirely a sulphide of iron, FeS_2 . These bodies often contain gold and silver.

ACTION OF HEAT AND AIR ON SULPHIDES.

Most sulphides melt when strongly heated out of contact with air, and some of them are converted into vapour; but no other change is observed. If air is present, another change takes place where the air comes into contact with the sulphide. It is a surface change, and proceeds most rapidly when the material is finely divided, and the temperature is kept below the point at which the particles soften and clot together. If the action is continued until no further change takes place the sulphur disappears, and its place is largely taken up by oxygen. The *sulphide* is thus converted into *oxide*. There are some exceptions to this statement, but it is generally true. It is noticed that as the action proceeds the material gets more and more infusible, till finally it can be raised to a bright red heat without partial fusion or clotting. This is because oxides are generally more infusible than the corresponding sulphides from which they are formed. The above operation is technically known as **roasting**. This kind of work requires a muffle furnace to be properly carried out, and is fully dealt with in works on metallurgy; but some useful information can be obtained by simple experiments about general and intermediate changes.

EXP. 28.—Put a little finely-powdered iron pyrites into a small test-tube, and carefully heat the tube in the Bunsen flame. Sulphur vapour is given off, which condenses to liquid on the sides of the tube, and finally solidifies. A residue is left at the bottom of the tube, which resembles the iron sulphide of Exp. 27.

EXP. 29.—Put a little pyrites into the middle of a piece of glass tube open at both ends; hold the tube in a slanting position over the Bunsen flame, so that the pyrites is heated. A pale blue flame is seen over the heated powder. The position of the tube encourages air to pass in at the bottom, through the tube, and out at the top. The sulphur driven out of the pyrites by the heat burns in the oxygen of the air passing through the tube, and the smell of burning sulphur is readily detected in the gas issuing from the top.

It should be noted here that iron pyrites, FeS_2 , contains twice as much sulphur as common iron sulphide, FeS , but that half of it is more loosely held, and is driven off when the compound is heated, leaving the simpler compound as a residue.

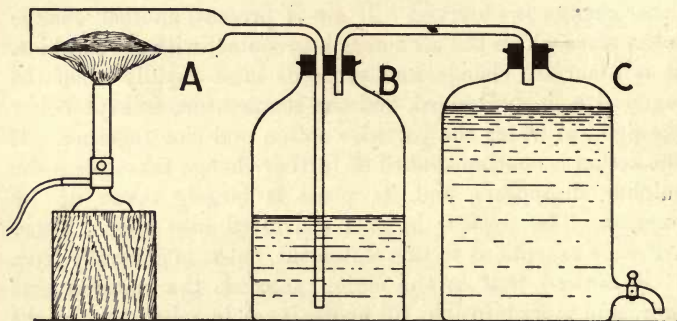
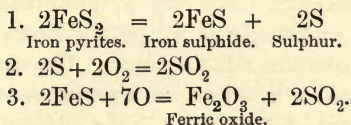


FIG. 16.

EXP. 30.—Fit up the apparatus shown in Fig. 16. A is a piece of combustion-tube about 5 inches long, drawn off at one end, and connected with the bottle B, which contains a little water. The aspirator C, which is simply a large bottle with a tap at the bottom, is nearly filled with water, and connected with B by a flexible tube. When the tap at the bottom of C is opened water runs out, and air passes through A and B into C to take its place. The rate at which air flows through A can be regulated by the tap, and a steady current thus kept up. If now some iron pyrites is put into A,

and heated by a Bunsen flame underneath, while a current of air is aspirated over it, a blue flame is seen in the tube, and white fumes appear in B. The action may be continued for ten minutes, then stopped, the bottle B removed, and the fumes blown out. The water smells strongly of sulphur dioxide, which proves that one of the changes resembles the burning of sulphur in air.

If the roasting is continued long enough the whole of the sulphur is practically removed, and the residue, which is bluish black in colour, is found to be an oxide of iron, having the formula Fe_2O_3 . Now part of the sulphur of the pyrites, FeS_2 , is driven off by heat alone, leaving FeS . See Exp. 28. The remainder is removed by the direct action of the oxygen of the air. The various changes are expressed by the equations :



Sulphuric Acid, H_2SO_4 .—By special means it is possible to make the sulphur dioxide take up a further proportion of oxygen from the air. It is thus converted into another definite compound, *sulphur trioxide*, SO_3 , a white volatile solid, which unites readily with water.

EXP. 31.—Fit up apparatus similar to that shown in Fig. 16, but insert a loosely-fitting plug of asbestos, the fibres of which have been coated with finely-divided platinum. The position of the plug is shown in Fig. 17. Put some coarsely-powdered iron pyrites, or sulphur, in the open end of A (Fig. 16), heat it with the Bunsen flame, and heat the asbestos at the same time with a separate burner. Aspirate a moderate current of air through the apparatus. The sulphur dioxide formed by the roasting of the pyrites, or the burning of the sulphur, is drawn,

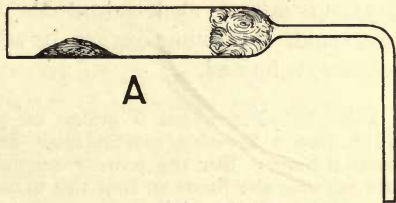
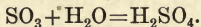


FIG. 17.

together with the excess of air, through the hot platinized asbestos. A should not be less than 1 inch internal diameter, and the quantity of sulphide limited. A little added from time to time gives the best results. As the air is only partially exhausted when it reaches the asbestos, the sulphur dioxide takes up more oxygen, and is converted into the trioxide. Dense white fumes now appear in B, and readily dissolve into the water present. The last change is expressed thus :



Remove the bottle B, move it about so as to make the liquid run over the whole surface, drain it into a porcelain evaporating-dish, and heat it carefully over the Bunsen flame until white fumes appear. When cold the dish is found to contain a small quantity of an oily liquid with very powerful acid properties, and resembling in every way oil of vitriol, or sulphuric acid, H_2SO_4 .

The pure acid is a heavy oily liquid of definite composition, which mixes with water in all proportions. The commercial acid usually contains a little water. The manufacture of the commercial acid is based on the changes described above, but oxygen is carried from the air to the sulphur dioxide by means of oxides of nitrogen (Chap. VII.). The plant required for its economical production is very extensive, and a detailed account of the process will be found in any of the larger works on chemistry.

It has been assumed that in roasting a sulphide the whole of the sulphur is converted into sulphur dioxide, and its place in the sulphide taken up by oxygen. In this case an oxide of the metal is formed ; but if the temperature is kept down, oxygen is actually absorbed into the mass, and a more complex compound, containing oxygen in addition to the metal and sulphur, is formed.

Exp. 32.—Put about 5 grams of powdered copper sulphide, Cu_2S , into a fire-clay roasting-dish, and place the dish over the Bunsen flame. Stir the powder constantly with an iron scraper, and regulate the flame so that the mass just softens, but does not clot sufficiently to stick to the dish. Continue the roasting for twenty minutes, or longer, if time permits. Transfer the residue to a porcelain mortar, and grind it to a powder again. Boil the powder for a minute or two in 20 c.c. of water contained in a small

beaker. Filter the solution into a clean porcelain dish, and, if it is deep blue in colour, set it aside to crystallize; if not, drive off some of the water by boiling the solution over a small flame before setting it aside. Boil up a little of the raw sulphide with water in a test-tube, and notice that the solution remains colourless.

Blue crystals are obtained, which are readily seen to be similar to the crystals of commercial blue vitriol. The changes by which the new compound is formed are somewhat complex, and cannot be considered at this stage; but the final result is equivalent to an absorption of oxygen by which copper sulphate, CuSO_4 , is produced.

Percentage Composition.—The usual way of expressing the composition of a compound, after it has been experimentally obtained, is to put it into the form of percentages. This is known as percentage composition.

EXAMPLE.—To find the percentage composition of copper sulphide from the data given with Exp. 26.

2.507 grams of copper sulphide contain 2 grams of copper;

\therefore 1 gram of copper sulphide contains $\frac{2}{2.507}$ grams of copper;

\therefore 100 grams ,, ,, contain $\frac{2 \times 100}{2.507} = 79.77$ grams of copper.

Similarly for sulphur $\frac{0.507 \times 100}{2.507} = 20.22$ grams of sulphur.

Therefore the percentage composition is $\begin{cases} \text{Cu} = 79.77 \\ \text{S} = 20.22 \\ \hline 99.99 \end{cases}$

To find the formula of the compound, the percentage of each element is divided by its atomic weight, and each quotient so obtained is divided by the lowest quotient. The second division gives a series of numbers, from which it is easy to derive the formula. Thus—

$\frac{79.77}{63} = 1.25$, and $\frac{20.22}{32} = 0.631$; then $\frac{1.25}{0.631} = 2$ very nearly, and

$$\frac{0.631}{0.631} = 1.$$

The required formula is Cu_2S .

The method of finding the formula of a compound depends upon: (1) the invariable proportions of the elements in the compound; (2) the existence of atoms, which for the same element are of invariable weight. If, then, it is found that certain weights of two or more elements combine to form a compound, and the idea of atoms is applied, the only inference which can be drawn is, that the weight of any one of the elements is made up of an enormous number of similar atoms. And it is evident that if the atomic weight is known, the relation between it and the known weight of the element in the compound is proportional to the number of atoms in that weight.

Thus the ratio $\frac{79.77}{63} = 1.25$ is proportional to the number of atoms in 79.77 parts of copper, and the ratio $\frac{20.22}{32} = 0.631$ is proportional to the number of atoms in 20.22 parts of sulphur.

Results obtained in this way lead to what are called *empirical formulæ*, for they only give the ratio between the numbers of the different atoms in the molecule of the compound. Thus Cu_2S might be written Cu_4S_2 , Cu_6S_3 , etc. It is, however, the only method of obtaining formulæ which is applicable to all compounds without exception. Other facts have to be taken into consideration in deciding as to the actual number of atoms in the molecule of a compound; and, as they are not applicable generally, there are many compounds the actual molecular formulæ of which are not known.

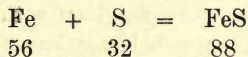
SUMMARY.

The matter of this chapter should receive careful attention, especially that portion which refers to the determination of formulæ and the formation of equations. So much depends upon getting clear ideas of the quantitative relations between

the elements in a compound, that it is hardly possible to devote too much attention to it at first. Some difficulty is always experienced by those who are not acquainted with the use of symbols in general, in their endeavour to grasp the meaning of a formula or of an equation. The facts of a particular reaction and the attempt to explain them are sometimes confused ; so that it is a good plan to get the facts well digested before attempting their explanation.

The formation of sulphides, and the method of finding their formulæ, should be carefully studied. The exact composition of a compound can be found, either by building it up from its elements (synthesis), or by separating it into its elements (analysis). This is the first step, and whichever method is adopted, both the nature of the elements in the compound and their proportions by weight must be determined. Very often it is possible to employ both methods for the same compound, in which case they must confirm each other. Any number of experiments, however diverse they may be, if they are directed to the determination of the composition of a given compound, should lead to the same result.

The distinction between the facts of a particular reaction and the theoretical considerations used in their explanation is well brought out by studying the equation :



The *fact* is that 56 grams of iron will combine with 32 grams of sulphur to form 88 grams of iron sulphide. The *theory* states, in scarcely less definite language, that for every atom of iron in 56 grams of the metal there is a companion atom of sulphur in 32 grams of that element ; that these atoms run together in pairs to form molecules of iron sulphide ; and that whatever takes place between a single pair of atoms is simply repeated with every other pair in the reacting mass.

This is equivalent to saying that whatever may be the

number of atoms in 56 grams of iron, there is the same number of atoms in 32 grams of sulphur.

In practice, then, the symbols represent measurable proportional weights of the elements. Theoretically they represent single atoms, and one side of an equation shows a group containing the minimum number of atoms which can take part in the chemical change represented by the equation, the other the result of the change. Then, however great the reacting mass may be, it is divided up into similar groups as the change proceeds, and any excess of one kind of atoms over the others takes no part in it.

QUESTIONS.

1. What changes take place when sulphur is heated out of contact with air?

2. How may copper be converted into its sulphide? Describe the experiment.

3. Write down a chemical equation, and say in your own words what you think it means.

4. How may sulphuric acid be prepared from sulphur? State the general properties of the acid.

5. What takes place when a sulphide is heated in air?

6. What is understood by the percentage composition of a compound? From the example given with Exp. 27 find the weights of iron and sulphur in 100 grams of the sulphide, and from the percentages so obtained deduce the formula of the compound.

7. The empirical formula of a compound does not always represent its molecule. Why is this?

CHAPTER VI

COMMON ELEMENTS AND COMPOUNDS

Common Salt.—This well-known substance is found in the earth in various parts of the world. The most extensive deposits in this country are found in Cheshire, Worcestershire, and Yorkshire. It also forms the bulk of the dissolved matter in sea water. It is a white solid which dissolves readily in water, and crystallizes from its solutions in cubes. The solid, or its solution, has a characteristic saline taste, by which it is readily recognised. As it is easily purified, the commercial salt is sufficiently pure for most purposes. Common salt, or sodium chloride, contains the metal sodium and the gas chlorine in the proportion of 23 parts of the metal to 35.5 parts of the gas by weight. Its formula is, therefore, NaCl .

Hydrochloric Acid.—This very important compound, as prepared for use, is a strongly-fuming liquid with very characteristic properties. It is known also as muriatic acid and smoking salts. The pure compound contains 1 part of hydrogen to 35.5 parts of chlorine by weight, and its formula is HCl . It is prepared from common salt.

EXP. 33.—Dry some common salt by heating it in an iron pan over the Bunsen flame. Make a dilute solution of sulphuric acid by pouring some of the strong acid slowly into its own volume of water. Notice that the solution becomes very hot, and remember that the acid must always be poured into the water, and not the water into the acid. Neglect of this rule may cause an accident. Put a little dry salt into a dry test-tube, add a little of the diluted acid, and warm the mixture over the Bunsen flame. A gas is

given off which fumes strongly in the air, and has a strong acid taste and smell. A strip of blue litmus-paper held in the fumes is turned red. The gas is hydrochloric acid.

EXP. 34.—Fit up the apparatus shown in Fig. 18. A is a 12-ounce flask fitted with a bung and angle-tube. B is a drying bottle containing a little strong sulphuric acid, and standing in a beaker of water to keep it cool. C is a gas cylinder with a delivery-tube. A and C are connected with B by flexible rubber tubes. D is a long-necked flask with a delivery-tube, and filled up to the mark with water. Put about 10 grams of dry salt into A, and add 50 c.c. of sulphuric acid (1 to 1); replace the bung, and heat the flask gently on a piece of gauze over the Bunsen flame. Gas is given off, passes

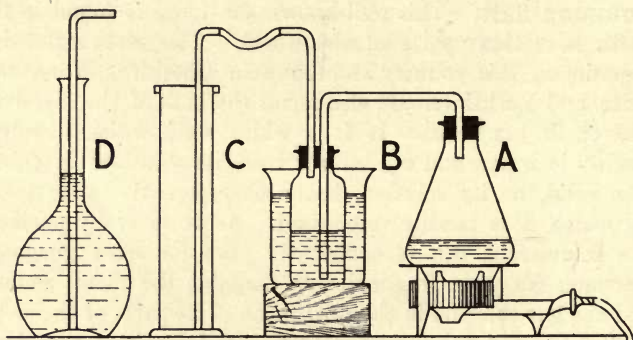
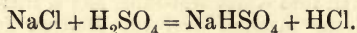


FIG. 18.

through the strong acid in B, which dries it, and collects in C by gradually displacing the air. White fumes will soon appear at the mouth of the jar, but a considerable quantity of the gas must escape before the whole of the air is expelled. When the jar is thought to be full remove the delivery-tube, and put a greased plate over the mouth of the jar. Fill another cylinder with the gas, and then connect B with the delivery-tube in the bottle D, which contains water up to the mark when the delivery-tube is in position. Allow the gas to pass into D until the water shows signs of running back. Disconnect from B, and note that the level of the water in D is considerably above the mark, the delivery-tube still being in position; also that the bottle feels warm to the hand.

The chemical change by which the gas is liberated is expressed by the equation :



The sodium hydrogen sulphate formed in the change remains in the flask, and is easily obtained as a crystalline solid from the residue.

Properties of Hydrochloric Acid.—The dry gas collected in the cylinders is colourless and transparent. On removing the plate from a jar of the gas, fumes appear at the mouth. The escaping gas, on coming into contact with moisture in the air, dissolves in it, and causes its condensation as an acid cloud.

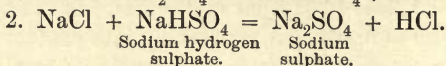
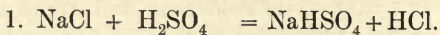
A burning candle held in a deflagrating spoon and carefully lowered into the gas ceases to burn, but just before the flame disappears the blue portion of it turns green. The gas is non-combustible, and does not support combustion.

A little blue litmus solution, when poured into the jar of gas used in the last experiment, is turned red, showing that the gas has acid properties.

When a jar of the gas is inverted over water and the plate removed, the water rushes up and fills the jar. The gas is very soluble in water, and as it is dissolved the water rises in the jar to take its place. The dissolution of the gas in the bottle D in Exp. 34 brings out two important facts: (1) that the volume of the solution is greater than the original volume of water; (2) that heat is developed during the dissolution of the gas. To be quite sure of the latter fact it is necessary to put the drying bottle B into a vessel containing cold water to ensure that cold gas passes into D. Also the weight of the solution is greater than that of water bulk for bulk, and increases with the quantity of gas absorbed, up to the point of saturation. The strong solution at ordinary temperatures has a density of 1.2, and contains 40 per cent. of HCl. To produce this the water dissolves more than 400 times its own volume of the gas. Thus the strong commercial acid contains, roughly, 40 parts by weight of the gas dissolved in 60 parts by weight of water.

Large quantities of the acid are obtained in the manufac-

ture of salt cake from common salt and sulphuric acid. The operation is conducted in a furnace, and at a higher temperature than that which can be used with a glass flask. In this case double the quantity of salt is decomposed by the same quantity of acid. The reaction takes place in two stages :



The gas is absorbed while passing through towers filled with coke over which water is allowed to trickle. The solution is collected in receivers at the bottom of the towers. The crude acid is often impure, and must be purified for special purposes, but the common acid is useful for many operations in which purity is not essential.

CHLORINE.

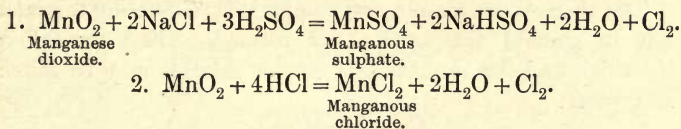
This element is a yellowish-green gas which is present in a number of compounds, of which common salt is the type. It can be obtained either from common salt or from hydrochloric acid. Black oxide of manganese, which is used in its preparation, is found in the earth as manganese ore or pyrolusite. Its formula is MnO_2 . It is a black, easily-powdered solid.

EXP. 35.—Well mix a little dry salt with some powdered black oxide of manganese. Put the mixture into a test-tube, add a little dilute sulphuric acid, and gently warm the tube. A yellowish-green gas is given off, which has a very irritating odour. The effect of the small quantity which gets into the air is quite perceptible. A piece of moistened litmus-paper held in the gas is quite decolourized. This yellowish-green gas which is liberated from the salt by the combined action of the oxide and the acid is chlorine, Cl_2 .

EXP. 36.—Use the apparatus shown in Fig. 18. The wash-bottle need not be kept cool. Put about 20 grams of black oxide of manganese into A, add 100 c.c. of strong hydrochloric acid, and heat the flask gently on the gauze. Allow the gas to collect in C until the jar seems full of a yellowish-green body. Cover the mouth with a greased plate. Collect several jars of the gas in the same way.

The experiment must be conducted in a fume-chamber, but if one is not available the gas should be collected over water. In that case a delivery-tube is passed directly from the flask A to a pneumatic trough, and under the mouth of an inverted cylinder filled with water. The gas is somewhat soluble in water, but if a rapid stream of it is kept up no difficulty is experienced in collecting a number of jars. Either the wet or dry gas can be used for illustrating most of its properties.

The changes taking place in the above experiments are expressed by the equations :



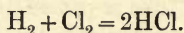
Properties of Chlorine.—It is a yellowish-green gas when seen by daylight, or by the light of burning magnesium, but the colour is too faint to be recognised by gaslight. It has a very irritating odour, and care should be taken not to inhale it in quantity. Fresh air is the best remedy.

Hydrogen or combustible bodies containing hydrogen burn in this gas, and finely-divided metals take fire when brought into contact with it.

Experiments with Chlorine.—1. Carefully lower a lighted candle, supported in the bowl of a deflagrating spoon, into a jar of the gas. It continues burning, but with a dull red, smoky flame, and a thin deposit of soot is formed on the inside of the jar.

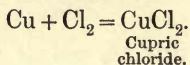
2. Moisten a piece of tow with turpentine, hang it on the bowl of a deflagrating spoon, and lower it into a jar of the gas. The turpentine suddenly bursts into flame, and a thick deposit of soot is formed inside the jar. The candle and the turpentine contain carbon and hydrogen, and, during the combustion the hydrogen only burns, the carbon being set free and deposited as soot. When the spoon is lifted out of the jar white fumes appear at the mouth. This

fuming is caused by the escape of hydrochloric acid gas. The change is expressed by the equation :



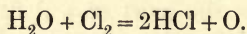
3. Grind some antimony to a fine powder in a mortar ; put it into a small bottle, and tie a strip of muslin over the mouth. Sprinkle some of the metallic powder into a jar of chlorine gas. A shower of brilliant sparks is seen. Repeat the last experiment, using finely-divided copper in place of antimony.

The changes are simple, and compounds resembling common salt in general composition are formed. They are called chlorides, and the formation of copper chloride may be taken as typical :



The conversion of metals into their chlorides is sometimes of considerable practical importance, and is effected on the large scale both by free chlorine and by common salt.

Chlorine is somewhat soluble in water, and forms a solution which smells strongly of the gas. When the solution stands for some time slow decomposition of the water takes place, with formation of hydrochloric acid and liberation of oxygen :



The change is more rapid in daylight, and very rapid when a body which will take up oxygen readily is put into the solution. On this account chlorine is sometimes called an oxidizing agent. Colouring matter of vegetable origin is readily decolourized by the gas in the presence of water. This action is called bleaching. It is probable that the oxygen liberated from the water combines with the colouring matter, and forms colourless compounds with it. Mineral colouring matter is not affected.

4. Moisten a strip of turkey-red cloth about half-way up

and suspend it in a jar of dry chlorine. The colour is rapidly discharged from the wet part, but very slowly from the dry portion.

Chlorine gas is made on the large scale, and absorbed into slaked lime to form bleaching powder, from which the chlorine is readily liberated for use. Common salt and chlorine are used in the metallurgy of copper, silver, and gold.

Potassium Chlorate, KClO_3 .—This useful compound may be prepared by passing chlorine gas into a strong solution of caustic potash. A thistle funnel, bent as shown in Fig. 19, is fitted to a wash-bottle containing a little water, and dips into the solution of potash in water (1 to 2). Chlorine, prepared as described above, is passed through the wash-bottle into the solution, by which it is rapidly absorbed. A crystalline solid separates from the solution. When the action is finished the liquid is allowed to stand for further separation, poured off, the solid dissolved in water, and recrystallized to purify it.

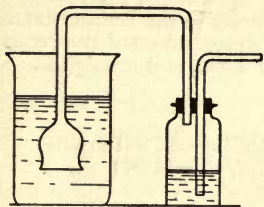
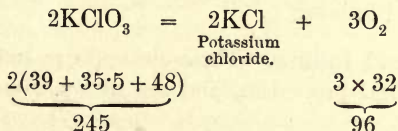


FIG. 19.

Action of Heat.—When potassium chlorate is heated it splits up into potassium chloride and oxygen, and this reaction is made use of in the preparation of moderate quantities of oxygen for experimental purposes.

EXP. 37.—Put a little powdered chlorate into a dry test-tube, and heat it strongly in the Bunsen flame. It melts and gives off bubbles of gas, which, when tested by the introduction of a glowing splint, is found to be oxygen.

The complete change is expressed thus :



By mixing the salt with about a quarter its weight of manganese dioxide, and heating the mixture, the gas is liberated much more freely and at a lower temperature. The oxide undergoes very little change, and its action need not be considered now.

EXP. 38.—Thoroughly dry some powdered potassium chlorate in a porcelain basin on the sand-bath. Heat some powdered black oxide of manganese in a porcelain crucible over the Bunsen flame. Weigh accurately 2 grams of the dry chlorate, and put it into a dry test-tube; add about the same weight of the ignited black oxide, and well mix the two by careful shaking. Now weigh the tube and its contents accurately, and then heat it gently in the Bunsen flame until no more gas is liberated. Two or three minutes' heating is usually sufficient. Allow the tube to cool down, and reweigh it.

EXAMPLE.

| | | | | |
|--|---|---|-------|--------------|
| Weight of tube and mixture before heating=15·641 grams | | | | |
| “ | “ | “ | after | “ =14·863 “ |
| Loss | | | | =00·778 gram |

The loss is due to the escape of oxygen from the 2 grams of chlorate, and may be compared with the loss calculated by using the weights given in the equation on p. 75.

$$\begin{array}{rcll} \text{For 245 grams of KClO}_3 \text{ lose 96 grams of O}_2 & & & \\ \therefore 1 \quad \text{“} \quad \text{“} \quad \text{“} & \frac{96}{245} & & \\ \therefore 1 \quad \text{“} \quad \text{“} \quad \text{“} & \frac{96 \times 2}{245} = 0\cdot784 \text{ gram of O}_2. & & \end{array}$$

If the test-tube is fitted with a rubber bung and delivery-tube, and is supported in a horizontal position by a clip, the evolved gas may be readily collected over water. This method is often used to obtain oxygen for experimental purposes, and will be referred to later.

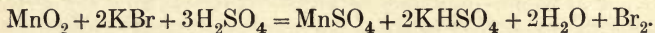
Bromine and Iodine.—These elements resemble chlorine in their chemical properties, and are of considerable use in the laboratory.

Bromine is a dark red, heavy liquid, 3.18 times heavier than water. It gives off a red vapour at ordinary temperatures, which is even more irritating than chlorine. It is somewhat soluble in water, forming a red solution. It attacks water in the presence of bodies which will take up oxygen, and on that account is useful indirectly as an oxidizing agent. The commonest compound of bromine is potassium bromide, KBr.

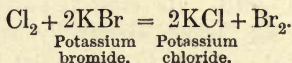
Iodine is a greyish-black crystalline solid which melts readily, and gives off a violet vapour with an irritating odour. It volatilizes slowly at ordinary temperatures, so that even the solid has an acrid smell. Its most important compound is potassium iodide, KI, which is readily soluble in water. Iodine is only slightly soluble in water, but is readily soluble in water containing potassium iodide, and is often used in this form. It also dissolves readily in alcohol, ether, and carbon bisulphide.

Compounds of bromine and iodine are present in small quantities in sea-water, and are absorbed into sea-plants during their growth. When dry seaweed is heated to a low red heat in a retort, combustible gas is driven off, and a black residue left, which, on treatment with water, yields a solution containing a considerable quantity of dissolved matter. On careful evaporation in pans, potassium sulphate crystallizes out, and is separated from the hot solution; on cooling the hot liquid a further deposit of potassium chloride is obtained. The remaining solution, called the mother-liquor, contains compounds of bromine and iodine, and, after mixing with sulphuric acid and standing for a time, is transferred to an iron still, in which it is heated with black oxide of manganese. Iodine distils over, and is condensed in receivers in the solid state. When no more iodine passes over more black oxide is added, and the heating continued. Now bromine distils over, and is collected in a fresh set of receivers in the liquid state. The bromine so obtained is usually sufficiently pure for ordinary purposes, but the iodine needs purification.

It will be noticed that the same materials are used to liberate bromine and iodine as are used in Exp. 36 for the liberation of the chlorine from common salt, and the chemical changes taking place are also similar. Compare the equation given below with No. 1 on p. 73:



In Germany bromine is largely prepared by the action of chlorine on bromides in the mother-liquor after the separation of potassium chloride from the mixed potassium salts which occur in the Stassfurt salt-beds. The reaction is simple:



Saltpetre, also called nitre or potassium nitrate, is obtained in the form of colourless crystals, or as a white powder. It is very soluble in water, and the solution has a saline taste. An efflorescence which appears on the surface of the soil in hot countries, notably in India, is found to consist largely of potassium nitrate. If this surface layer is stripped off and treated with water, the nitrate dissolves, and may be recovered from the solution by crystallization. The formation of the nitrate is brought about by changes in the organic matter of the soil in the presence of decomposing rocks containing potassium compounds. And it is only where these conditions are present that the compound is formed. There is also a method, based upon similar changes, for its artificial production. The corresponding compound, Chili saltpetre or sodium nitrate, occurs as large deposits in certain parts of South America. This compound is very similar in its properties to the potassium salt, and, as it is cheaper, is used for some purposes in place of the latter.

The formulæ of the compounds are KNO_3 and NaNO_3 respectively.

Nitric Acid, HNO_3 .—This compound is a strongly-fuming liquid with very powerful properties. It is readily obtained

from either of the nitrates described above by acting upon them with strong sulphuric acid.

EXP. 39.—Fit up the apparatus shown in Fig. 20. A is a glass-stoppered retort of about 8 ounces capacity. B is a small flask resting in a bowl of water, and covered with wet blotting-paper to keep it cool.

Put about 20 grams of powdered saltpetre into the retort, and pour in strong sulphuric acid through a funnel until the solid is well covered. Replace the stopper, and gently heat the mixture. Reddish vapours appear in the retort; drops of liquid

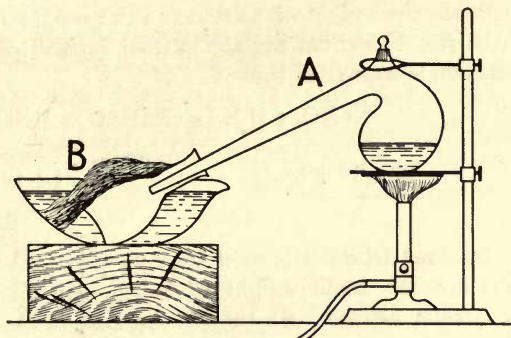
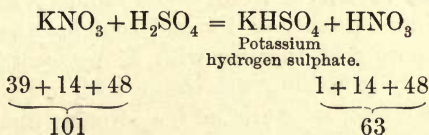


FIG. 20.

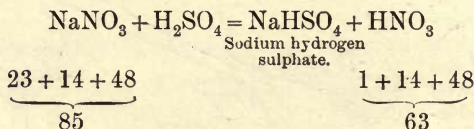
collect in the stem and run down into the receiver. Continue the heating for twenty minutes. Then remove the receiver and examine the liquid which has distilled over.

The acid formed by the reaction in the retort is gaseous at the temperature of the experiment, and, passing in this form into the cooler stem, condenses there, and runs into the receiver. The liquid thus collected is usually coloured, which is due to the presence of gaseous impurities formed by the decomposition of part of the acid by heat. If a stream of air is blown through it for some time, the colour disappears, and a colourless, strongly-fuming liquid is obtained.

The change taking place in the retort is expressed by the equation :

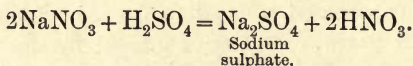


The potassium hydrogen sulphate is left as a residue in the retort. The conversion of the nitrate into nitric acid is easily seen to consist of an exchange of hydrogen for potassium. Reference to the table of atomic weights will show that the numbers under the formulæ in the equation represent the molecular weights of the compounds, and also the proportion between the weight of nitrate and the weight of acid formed from it. If sodium nitrate is used instead of saltpetre, the reaction is expressed thus :



On comparison it is seen that 85 parts of sodium nitrate produce the same weight of nitric acid as 101 parts of potassium nitrate. So that if the acid is the object of the preparation, the sodium compound is the more economical to use.

In the manufacture of the acid Chili saltpetre is used, and the reaction is conducted in iron retorts lined with fire-clay. A much higher temperature is employed and twice as much acid obtained with a given weight of sulphuric acid. This is explained by the equation :



The acid vapour is condensed in a series of earthenware receivers, and afterwards decolourized by blowing a current of air through the liquid.

Properties of Nitric Acid.—The ordinary strong commercial acid has a density of 1.4, and contains about 65 per cent. of the pure acid, together with 35 per cent. of water. But by carefully redistilling this strong acid, mixed with half its volume of strong sulphuric acid, a strongly-fuming liquid

is obtained. This is the practically pure acid, containing 100 per cent. HNO_3 , and having a density of 1.53. So that pure nitric acid is a colourless liquid, which is readily vapourized and easily decomposed. It is much more stable in the presence of water, with which it mixes in all proportions.

A dilute solution of the acid turns blue litmus red, and has the characteristic sour taste of acids in general. The strong acid has a very caustic action upon the skin, which turns yellow, then black, and finally peels off. It is a powerful oxidizing agent, readily giving up part of its oxygen to bodies which will absorb that element. Sodium and potassium nitrates are similar to the acid in this respect.

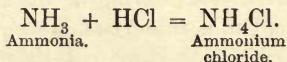
EXP. 40.—Make a piece of charcoal red-hot in the Bunsen flame, place it on a tile, and carefully pour a few drops of strong nitric acid upon the incandescent part. The glowing charcoal glows more brightly, showing that increased oxidation is taking place, due to the extra supply of oxygen obtained from the acid.

EXP. 41.—Melt a little saltpetre in a test-tube supported by a clip, and drop in a small piece of charcoal. When the charcoal begins to burn, remove the flame, and the combustion will continue. The charcoal burns brightly in the oxygen derived from the nitrate.

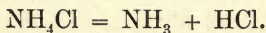
Repeat the last experiment, but drop into the tube a small piece of sulphur instead of charcoal. The burner may be removed before dropping in the solid, as the combustion commences at once and continues vigorously. An iron tray should be placed under the tube, as the heat developed is sometimes sufficient to fuse the bottom and cause it to drop out.

Ammonium Chloride.—One of the by-products of the manufacture of coal-gas is known as ammoniacal liquor. When this liquid is mixed with lime and heated in a closed vessel, ammonia gas is liberated, which is readily absorbed by strong hydrochloric acid and converted into ammonium chloride. As the acid liquid becomes saturated, the chloride crystallizes out,

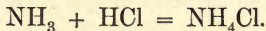
is collected, purified, and put on the market as sal-ammoniac. The reaction is :



The pure compound is a white, crystalline, odourless solid, readily soluble in water. It passes directly from the solid to the gaseous state when heated. In the gaseous state its molecules are largely split up into ammonia and hydrochloric acid molecules :



But these recombine as the temperature falls, and the original solid is reproduced :



This splitting up of the molecules at or above a definite temperature, and their recombination below that temperature, is known as **dissociation**. The last change is readily shown by filling two gas-jars with the dry gases and bringing them together mouth to mouth. The white chloride forms rapidly and deposits on the sides of the jars.

Ammonia Gas, NH_3 .—This compound has a very pungent odour, and its presence is very readily detected, although it is quite transparent and colourless.

EXP. 42.—Mix together 5 grams of ammonium chloride and 4 grams of quicklime; put the mixture into a test-tube fitted with a bung and a straight delivery-tube about 8 inches long; fix the test-tube in a clip in the vertical position, and invert a wide test-tube over the delivery-tube so as to rest on its end. Now heat the mixture, and allow the gas to collect in the inverted tube. When the tube is full, which is readily detected by the rapid escape of the gas from the mouth, replace it by a fresh one, and make an experiment with the full tube.

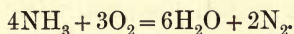
The heating of the mixture need not be continued during the testing of the gas. Tests may be made to prove the following statements :

1. If a piece of red litmus-paper is held in the gas, it is turned blue. The gas has, therefore, alkaline properties.

2. If a burning match or taper is put into an inverted tube filled with the gas, the flame disappears, and the gas does not take fire. It is non-combustible, and a non-supporter of combustion under ordinary circumstances. If the gas is heated strongly, or is mixed with oxygen, it burns with a somewhat feeble, yellowish flame; water is formed, and nitrogen liberated.

3. If a well-filled tube of the gas is placed mouth downwards in a dish of water, the liquid rises in the tube to take the place of the dissolved gas, which is very soluble in water. A piece of red litmus-paper dipped into the water before the dissolution is unchanged; but if dipped in after, is turned blue.

4. If a piece of clay tobacco-pipe is connected with the delivery-tube by flexible rubber, and its end is strongly heated in the Bunsen flame, while a current of gas is driven through it by heating the mixture, the gas burns at the hot end of the clay pipe. The change is:



The solubility of ammonia is its most remarkable property. Cold water will absorb upwards of 1,000 times its own volume of the gas. The ordinary ammonia liquor is simply a strong solution of the gas, and has many useful applications. The alkaline character of the solution, and the readiness with which the gas escapes from it, has earned for the compound the name of the **volatile alkali**.

The principal **fixed** alkalies are caustic potash and caustic soda, and their solutions in water have properties very similar to those of ammonia solution. But they are both solids, which can be melted and raised to a high temperature without decomposition. The result, then, of evaporating separate solutions of these three alkalies would be a clean vessel for the first, and solid residues for the other two. All three, however, neutralize acids, turn litmus blue, or methyl orange yellow, and have a caustic action on the skin.

The formulæ for caustic soda and caustic potash are NaHO and KHO , and, by analogy, the formula of the compound of ammonia supposed to be present in its solution is written $(\text{NH}_4)\text{HO}$, or NH_4HO .

Using the systematic names, the following comparison can be made :

NaHO , sodium hydroxide.

KHO , potassium hydroxide.

$(\text{NH}_4)\text{HO}$, ammonium hydroxide.

The group (NH_4) , although it has no free existence, plays an important part in ammonium compounds. It resembles an atom of sodium or potassium in its chemical functions, and is called a compound radicle on that account.

SUMMARY.

Common salt, saltpetre, and black oxide of manganese are found ready to hand in Nature, and, in conjunction with sulphuric acid, are used in the preparation of other equally important compounds and elements. The common acids are exceptionally important in the treatment of metals. Ammoniacal gas liquor is the usual source of ammonia and ammonium compounds.

QUESTIONS.

1. Explain what takes place when common salt is heated with moderately strong sulphuric acid. Sketch the apparatus used.
2. How is chlorine gas prepared, and what are its most important properties? Describe briefly the properties of its companion elements.
3. What happens when potassium chlorate is heated—
(a) alone, (b) mixed with black oxide of manganese?
4. How is nitric acid prepared?
5. Give a short description of the three common acids.
6. Write a short description of ammonia and its compounds.

CHAPTER VII

METALS AND ACIDS

THE common forms of hydrochloric, nitric, and sulphuric acids are now familiar, and their more evident properties have been sufficiently studied to enable them to be handled intelligently. The relation between metals and the common acids is an important one, and the study of the reactions which take place when they are mixed together can now be profitably undertaken. In many cases a very marked change takes place, which is readily noticed, and often easily investigated. But in some cases no change is effected, and the metal and acid may be left together for any length of time without alteration.

Exp. 43.—Put small pieces of zinc, tin, and platinum into three test-tubes, and add to each 5 c.c. of dilute nitric acid. Warm the tube, if necessary, to start the action, and note all the changes which take place.

The acid which is added to the zinc boils up, and a rapid escape of bubbles of gas is observed. The metal entirely disappears.

The tin changes to a white powder, and a red gas with an acrid odour is given off.

The platinum is apparently unchanged, and, if weighed before and after the experiment, is found to be the same.

Two practical problems now present themselves: The first is to learn as much as possible about the liberated gas; the second is to find out what happens to the metal.

TO FIND THE VOLUME OF GAS EVOLVED WHEN A WEIGHED PIECE OF METAL IS DISSOLVED IN AN EXCESS OF DILUTE ACID.

The apparatus shown in Fig. 21 is to be fitted up. A is an 8-ounce flask fitted with a rubber bung and an angle-tube. B is a 12-ounce bottle fitted with a rubber bung and two angle tubes. C is a gas-cylinder of about 500 c.c. capacity. B is connected with A and with the delivery-tube *d* by pieces of sound, well-fitting rubber tube about 4 inches long. These

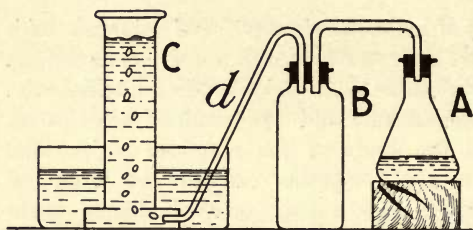


FIG. 21.

flexible connections allow the bung to be removed from or inserted in the neck of A, and the delivery-tube *d* to be raised above B without disturbing the

apparatus. Any form of pneumatic trough may be used, but one with a beehive shelf is very convenient. The apparatus must be perfectly gas-tight, so that care should be exercised in the selection of the fittings and in the fitting up, or poor results will be obtained. When ready, the apparatus may be used for several experiments in succession, as a single experiment requires a few minutes only for completion.

METALS AND HYDROCHLORIC ACID.

Zinc—Exp. 44.—Use the apparatus shown in Fig. 21. Add a little water to the flask B, shake well so as to wet the sides, allow it to stand for a minute, and then pour out the excess of water. Remove the bung from the flask A, and add 25 c.c. of dilute hydrochloric acid (1 to 1). Cut a strip of zinc foil about 1 gram in weight, and weigh it accurately. Fill the cylinder C, invert it on the shelf of the trough, and arrange the end of the delivery-tube under its mouth. Examine the connections to see that they are well made, as the experiment is a failure if the whole of the expelled gas is not collected in C. Drop the weighed metal

into A, and rapidly insert the bung. If, when the action has ceased, the flask A is warm, due to the heat evolved during the dissolution of the metal in the acid, place it in a shallow pan containing water which has been standing in the laboratory for some time. This will quickly bring the flask and its contents back again to the original temperature, especially if the flask is moved about in the water. When the level of the water in the delivery-tube is constant, raise the tube and allow the liquid to run back into B. Pour the water from B into a 50 c.c. measure, and note its volume. This is the measure of the excess of gas driven into C by the increase in the temperature in A. Now moisten a narrow strip of filter-paper, and fix it on C a little above the water-level in the cylinder; depress the cylinder in the trough until the water-level is the same inside and outside; move the paper till its lower edge marks this level. Remove the cylinder from the trough, and put a lighted taper to its mouth. The gas is a mixture of air and hydrogen, and burns with a slight explosion. Now fill the cylinder to the mark with water, rinse out the 500 c.c. measure, pour in the water from the cylinder, and note its volume. This is the measure of the volume of gas collected in C, and, therefore, of the volume of gas liberated from the acid by the weighed quantity of zinc, which must displace that volume from A and B.

Further information about the experiment is obtained by noting the height of the barometer column, which gives the pressure of the gas, and by taking the temperature of the water in the trough with a thermometer, which is also the same as the temperature of the gas collected over it. For the volume of a gas varies considerably with variations of its temperature and pressure, and is increased by the presence of water vapour in it. In accurate determinations it is necessary to reduce this volume to that of the dry gas at the normal temperature and pressure (N.T.P.). But the beginner may leave this for a time. A series of experiments has shown that an approximate correction for the volume of a gas collected over water under ordinary laboratory conditions is obtained by multiplying the observed volume by 0.916.

| | | |
|-------------------------------|---|----------|
| EXAMPLE.—Weight of zinc taken | = | 1 gram. |
| Volume of gas collected in C | = | 375 c.c. |
| „ water in B | = | 3 „ |
| „ gas liberated | = | 372 „ |

Then $372 \times 0.916 = 340.7$ c.c. = the volume of dry hydrogen at N.T.P. expelled from hydrochloric acid by 1 gram of zinc.

The weight of a litre of hydrogen has been determined with considerable accuracy, and may be used to find the weight of any given volume of the dry gas at N.T.P.

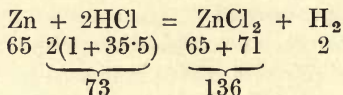
$$1 \text{ litre} = 1000 \text{ c.c.} = 0.0896 \text{ gram.}$$

Now, the volume of hydrogen liberated by 1 gram of zinc having been found, it is easy to calculate the volume liberated by 65 grams of the metal—*i.e.*, by an atomic weight of zinc in grams.

$$340.7 \times 65 = 22145.5 \text{ c.c.}$$

And, as each 1,000 c.c. of this gas weighs 0.0896 gram, the weight of the whole is $22145.5 \times 0.0896 \div 1000 = 1.984$.

The number thus obtained from a rough experiment is sufficiently near the whole number 2 to suggest that an atomic weight of zinc in grams liberates 2 atomic weights of hydrogen in grams. From the formula HCl it is seen that 2 molecular weights of hydrochloric acid in grams are required to supply the 2 grams of hydrogen, and as the whole of the chlorine combines with the zinc, the complete change is expressed by the equation:

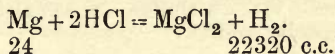


Magnesium—Exp. 45.—Weigh 0.3 gram of magnesium ribbon or wire. Add 50 c.c. of dilute hydrochloric acid (1 in 20). Make the magnesium into a coil, drop it into the flask, and quickly replace the bung. The gas comes off rapidly. Follow the instructions given for Exp. 44, and make the necessary measurements. Prove that the liberated gas is hydrogen.

| | | | |
|-----------|--------------------------|---|-----------|
| EXAMPLE.— | Weight of magnesium used | = | 0.3 gram. |
| | Volume of gas in C | = | 312 c.c. |
| | „ water in B | = | 7 „ |
| | „ gas liberated | = | 305 „ |

NOTE.—The principles upon which the above calculations are based will be found in the Appendix.

Then $305 \times 0.916 = 279.4$. Compare this result with the equation :

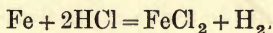


Iron.—The dissolution of this metal is less rapid than that of zinc or magnesium, and, when the evolution of the gas slows down, it is necessary to heat the flask. This can be done by placing it on gauze over a circular Bunsen burner. The flexible connection between A and B, Fig. 21, enables this to be readily done. The heating is continued over a small flame until bubbles of gas cease to escape from the delivery-tube, or escape very slowly. As commercial iron contains impurities, the volume of gas liberated by a given weight of the metal falls a little short of that which would be obtained by using the pure metal.

EXP. 46.—Weigh 0.7 gram of clean iron filings; transfer it to the flask A, Fig. 21; add 25 c.c. of strong hydrochloric acid, and rapidly replace the bung. When the action slows down, heat the flask gently until the dissolution is finished. Cool the flask and make the necessary measurements. Prove that the gas is hydrogen. During the heating a considerable volume of air will be expelled from the flask, and a much larger quantity of water will run back into B. When the bung is removed from A an offensive smell will be noticed, which is due to the action of the acid on the combined carbon present in the iron.

| | | |
|-------------------------|---|-----------|
| EXAMPLE.—Weight of iron | = | 0.7 gram. |
| Volume of gas in C | = | 464 c.c. |
| „ water in B | = | 168 „ |
| „ gas liberated | = | 296 „ |

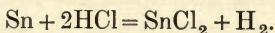
Compare the result with the equation :



Tin.—This metal dissolves even less rapidly than iron. The most suitable form for general use is the thin sheet metal, which is readily obtained by rolling down a piece of grain tin, or by hammering it out on a clean anvil.

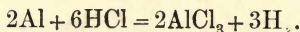
Exp. 47.—Weigh about 1·3 grams of tin ; add 20 c.c. of strong hydrochloric acid to A, Fig. 21 ; put in the metal, and heat the flask gently until the dissolution is complete. Measure and examine the gas collected in C.

The volume of gas obtained is a little greater than that given by the equation :



| | | |
|------------------------|---|--------------|
| EXAMPLE.—Weight of tin | = | 1·3 grams. |
| Volume of gas in C | = | 390 c.c. |
| „ water in B | = | 117 „ |
| „ liberated gas | = | <u>273 „</u> |

Aluminium.—The thin sheet metal is readily obtained, and dissolves in moderately strong hydrochloric acid without the application of heat. The change is expressed by the equation :



Exp. 48.—Weigh 0·3 gram of aluminium ; add 15 c.c. of dilute hydrochloric acid (1 to 1) to A, Fig. 21, and put in the weighed metal. The action is sufficiently rapid to finish without heating the flask, and very little water runs back into B. Measure and test the gas collected in C.

EXAMPLE.—0·318 gram of aluminium gave 426 c.c. of hydrogen ; or $426 \times 0·916 = 390·2$ c.c. of the dry gas at N.T.P.

Then, since 1,000 c.c. of hydrogen weigh 0·0896 gram, the weight of hydrogen which would be liberated by the dissolution of an atomic weight of the metal in grams is given by :

$$\frac{390·2 \times 0·0896 \times 27}{0·318 \times 1000} = 2·97 = 3 \text{ nearly.}$$

So that 1 atomic weight of aluminium displaces 3 atomic weights of hydrogen from the acid.

The metals used in the above experiments are those which are most readily acted upon by hydrochloric acid. Some common metals are dissolved very slowly, and others, again, are not attacked by the acid, even on prolonged heating. A metal which dissolves slowly may have its rate of dissolution increased by passing a current of air through the acid liquid.

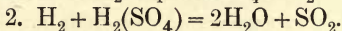
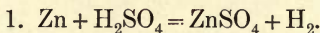
This is no doubt due to the formation of oxide of the metal by the oxidizing action of the air, and its dissolution by the acid.

It may be stated generally that hydrogen gas is set free when a metal dissolves rapidly in either hot or cold hydrochloric acid.

The compounds formed by the replacement of hydrogen in the hydrochloric acid molecules by the respective metals are called **chlorides**. They are readily separated from the solutions by evaporating the water and excess of acid, or by crystallization. (See Exps. 52 and 53.)

METALS AND SULPHURIC ACID.

When hydrochloric acid reacts with metals the general change is a simple one, corresponding to the simple character of the acid itself. But with sulphuric acid there is the possibility of secondary changes, for, if its molecules are regarded as consisting of the two groups H_2 and (SO_4) , the second group may undergo changes by which new compounds are formed. The simplest kind of change is when the group (SO_4) moves into or out of molecules in much the same way as an atom of an element does. This is the simple explanation of the ordinary dissolution of a metal in the dilute acid by which hydrogen is liberated. But when the acid is hot and concentrated, another reaction becomes prominent, by which sulphur dioxide gas is set free. The probable explanation of this is that, at the temperature used, a considerable proportion of the acid molecules are split up, or **dissociated** into (H_2) and (SO_4) groups, and that the hydrogen set free by the action of the metal on other acid molecules helps to attack the (SO_4) groups, and abstracts oxygen from them. This is expressed in the equations :



The experiments with dilute sulphuric acid are made in exactly the same way as with hydrochloric acid, so that a

detailed description will not be required. The dilute solution is made by pouring the measured quantity of strong acid into the measured quantity of water. The mixture is then stirred with a glass rod, and allowed to cool. The apparatus shown in Fig. 21 is to be used.

Zinc—EXP. 49.—Use about 1 gram of the thin sheet metal and 20 c.c. of dilute sulphuric acid (1 in 6). Measure and test the liberated gas.

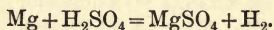
If the zinc is of good quality the action is very slow at first, and it may be necessary to warm the flask a little.

EXAMPLE.—1 gram of zinc gave $377 \times 0.916 = 345.3$ c.c. of hydrogen.

This result may be compared with that obtained by calculation from equation No. 1 on p. 19.

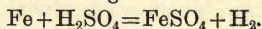
Magnesium—EXP. 50.—Use about 0.3 gram of the metal ribbon and 20 c.c. of dilute sulphuric acid (1 in 50). Measure and test the liberated gas.

EXAMPLE.—0.3 gram of the metal gave $305 \times 0.916 = 280.4$ c.c. of gas.



Iron—EXP. 51.—Use about 0.7 gram of the metal and 20 c.c. of the dilute acid (1 in 6). Heat the flask gently, as described in Exp. 46.

EXAMPLE.—0.7 gram of iron gave $296 \times 0.916 = 271.1$ c.c. of gas.



On comparing the volume of gas obtained with that determined by calculation from the equation, it is found to be deficient. This is due to the impurities in the commercial metal.

A comparison of the results obtained above shows that the volume of gas liberated depends upon the weight of metal used, and not upon the nature of the acid.

| ACID. | | Zn 1 GRAM. | Mg 0.3 GRAM. | Fe 0.7 GRAM. |
|-----------------------------------|----|------------|--------------|--------------|
| HCl .. | .. | 340.7 c.c. | 279.4 c.c. | 271.2 c.c. |
| H ₂ SO ₄ .. | .. | 345.3 ,, | 280.4 ,, | 271.1 ,, |

Thus the weight of sulphate formed is just as definite as the volume of hydrogen liberated. Similar experiments may be made with other metals and acids, with similar results.

PREPARATION OF HYDROGEN GAS.

The dissolution of zinc in dilute hydrochloric or sulphuric acid may be used as a source of hydrogen for experiments to demonstrate its properties. If the apparatus described on p. 24 is not available, this method is to be employed for obtaining a quantity of the gas.

EXP. 54.—A is a 12-oz. bottle fitted with a rubber bung, through which passes a thistle funnel, B, and a delivery-tube. About 10 grams of zinc is put into A, covered with water, and strong hydrochloric acid added through B, a little at a time. The gas is thus liberated steadily, and is collected in the cylinder C. The first jar of gas contains some air displaced from the generating-bottle; the gas collected after this is sufficiently pure for ordinary experiments.

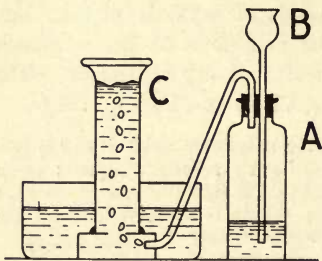


FIG. 23.

Experiments for demonstrating the properties of the gas are described on p. 25.

PREPARATION OF SULPHUR DIOXIDE.

As the action of concentrated sulphuric acid on metals is not susceptible of easy quantitative experiments, only one example will be given, and that the one commonly used to obtain sulphur dioxide in sufficient quantity to demonstrate its properties.

EXP. 55.—Fit up the apparatus shown in Fig. 24. A is a 12-ounce conical flask; B is a wash-bottle containing a little sulphuric acid (2 parts of acid to 1 part of water); C is a dry gas-cylinder. Put about 10 grams of sheet copper into A, and add 25 c.c. of strong

sulphuric acid. Heat the flask until the gas comes off freely, and then regulate the flame so as to obtain a steady stream of bubbles through B. Collect two jars of the gas by displacement of air, then transfer the delivery-tube to a bottle containing water, in which the gas will dissolve and form a solution. When the evolution of gas is nearly finished,

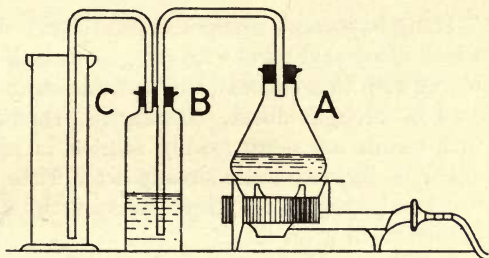
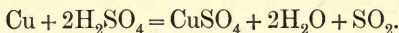


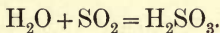
FIG. 24.

disconnect the apparatus and add 50 c.c. of water to the flask A; raise the contents to boiling, and filter the liquid into a porcelain dish. Concentrate the blue solution to about half its bulk by evaporation, and set it aside to crystallize. Blue crystals of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are obtained.

The principal change is expressed by the equation :



Properties of Sulphur Dioxide.—The gas collected in the jars is colourless and transparent, and has the odour of burning sulphur. When a burning candle is lowered into one of the jars, the flame disappears, and the gas itself does not burn. A solution of blue litmus is immediately turned red when poured into the jar. When the other jar is inverted over water and the plate removed, the water rises rapidly up the jar to take the place of the dissolved gas. The solution, made as described above, smells strongly of the gas, and is considered to contain sulphurous acid, H_2SO_3 , formed by the reaction between the gas and water, thus :



The pure acid has not been isolated; it is only known in solution, but it forms salts called sulphites.

METALS AND NITRIC ACID.

Many important changes depend upon the readiness with which nitric acid parts with oxygen to bodies capable of combining with that element, and an interesting series of reactions may be brought about. It may be remarked at the outset that metals are more readily soluble in nitric acid than in either of the two acids already dealt with. The metals may be roughly divided into three classes with respect to the action of nitric acid upon them.

1. The metal is converted directly into its oxide: Sn and Sb.

2. The metal is converted into a soluble nitrate: Cu, Mg, Hg, Pb, Fe, Ag, Zn.

3. The metal is not attacked by the acid: Au and Pt.

The solid non-metals also are more or less readily converted into oxides, which then combine with water to form the corresponding acids.

Tin—Exp. 56.—Heat a clean porcelain crucible over the Bunsen flame. When cold, weigh it carefully, and weigh in it 0.5 gram of tin. Add 5 c.c. of dilute nitric acid (1 to 1) from a pipette. Put a watch-glass over the crucible, and heat it carefully on the sand-bath or iron plate. When the action is finished, remove the watch-glass, and if any white particles adhere to it, rinse them into the crucible with a fine jet of water from the wash-bottle. Now place the crucible on a pipe-clay tripod (see Exp. 53), and evaporate the contents slowly to dryness. Then put the crucible in a pipe-clay triangle on an iron tripod stand, and heat it carefully with the Bunsen flame. Hold the burner in the hand, move the flame about, and be ready to remove it if the residue shows signs of spurting. When risk of loss is over, heat the crucible strongly for ten minutes, and then for a minute or two over the foot blow-pipe flame. If a muffle is available, it can be used for the final heating. When cold, weigh the crucible and oxide.

EXAMPLE.—Weight of crucible + oxide = 11.770 grams

 " " = 11.135 "

 " " = 0.635 gram

Then $0.635 - 0.5 = 0.135$ = weight of oxygen absorbed.

To find the formula of the compound we have : $\frac{0.5}{118} = 0.0042$
 and $\frac{0.135}{16} = 0.0084$. Therefore the ratio of the number of atoms
 of tin to the number of atoms of oxygen in the molecule is
 $\frac{0.0042}{0.0084} = 1 : 2$, and the formula is SnO_2 .

Antimony—Exp. 57.—Use 0.5 gram of powdered antimony, and 5 c.c. of dilute acid (1 in 3). Follow the instructions given for the last experiment. The final heating must be done with the crucible open, for if a lid is used, reducing gases may get into the crucible and cause loss by volatilization.

EXAMPLE.—Weight of metal used = 0.5 gram ; weight of oxygen absorbed = 0.138 gram. Use the data obtained to find the formula of the oxide. Sb = 120.

When metals dissolve in nitric acid their **nitrates** are formed. They are, however, readily decomposed on being heated, and, in most cases, are converted into the oxides of the contained metals. There are two notable exceptions to this: When nitrate of silver is heated it is completely decomposed, and a residue of metallic silver is obtained; when nitrate of mercury is heated it is first reduced to the oxide, which on further heating splits up into mercury and oxygen.

During the dissolution of a metal by nitric acid in an open vessel a red gas appears to be given off as long as any of the metal remains. If, then, the solution is evaporated to dryness, and the solid residue strongly heated, a further evolution of red gas is noticed. The final residue is found to be the oxide of the metal, and its weight compared with that of the metal used indicates the weight of oxygen absorbed.

Iron—Exp. 58.—Put 0.5 gram of clean iron wire into a weighed porcelain crucible, and add 5 c.c. of dilute nitric acid (1 to 1). Dissolve, evaporate, and heat the residue as described in Exp. 56. Allow the crucible to cool, and reweigh it. If the wire is thick, it should be first flattened under the hammer and rubbed with emery-cloth before being weighed and dissolved.

EXAMPLE.—Weight of metal used = 0.5 gram ; weight of oxygen absorbed = 0.215 gram.

Then $\frac{0.5}{56} = 0.0089$, and $\frac{0.215}{16} = 0.0134$. Therefore $\frac{0.0089}{0.0134} = 1 : 1.5$; or, taking the nearest whole numbers, the ratio is 2 : 3, and the formula of the oxide is Fe_2O_3 .

Mercury—Exp. 59.—Use about 1 gram of mercury and 5 c.c. of dilute acid (1 to 2). Proceed as in Exp. 58. After the evaporation, to obtain the white residue of nitrate, the crucible must be heated very carefully by holding the Bunsen burner in the hand and moving it about. The white colour of the residue gradually changes to red, and the action is finished when its colour is uniformly red. It must not become dark-coloured during the heating, or loss of metal and oxygen will take place. Reweigh the crucible when cold.

EXAMPLE.—Weight of mercury = 1.07 grams ; increase = 0.075 gram.

Find the formula of the oxide from the data thus obtained. $\text{Hg} = 200$.

Silver—Exp. 60.—Use 0.5 gram of silver and 5 c.c. of dilute acid (1 to 1). A residue = 0.5 gram of silver is obtained.

Similar experiments may be made with zinc, magnesium, lead, and bismuth. The result with the last-named metal leads to the formula Bi_2O_3 .

THE GASES EVOLVED WHEN METALS AND NITRIC ACID REACT.

It will be useful to consider, as far as can be done in an elementary way, the nature of the gases given off when metals dissolve in nitric acid. It has already been noticed that a red gas appears to be given off almost invariably when the dissolution takes place in an open vessel. But when the experiment is made in a closed vessel, it is found that the gas actually escaping from the liquid is not of constant composition for all metals. In fact, for the same metal even the volume and composition may vary with—(1) the concentration of the acid ; (2) the temperature at which the reaction is pro-

ceeding; (3) the depth of the layer of acid liquid above the dissolving metal, and through which the escaping gas has to pass. It also varies with the nature of the metal.

During the changes which nitric acid undergoes several oxides of nitrogen, and even nitrogen itself, may be liberated. The hydrogen of the acid is almost invariably converted into water by union with oxygen. Under exceptional circumstances it may be converted into ammonia, NH_3 , by union with nitrogen, or even liberated in the free state.

There are three well-known and easily-obtainable oxides of nitrogen: nitrous oxide, N_2O ; nitric oxide, NO ; and nitric peroxide, NO_2 , or N_2O_4 .

Nitrous Oxide, N_2O , is a colourless gas with a faint odour and sweet taste. It does not change when mixed with air, and is somewhat soluble in water. If a glowing splint is put into a jar of this gas, the splint bursts into flame; but when feebly-burning sulphur is brought into contact with it, the flame disappears. This test distinguishes nitrous oxide from oxygen. It is used by dentists to produce insensibility to pain for a short time. Its popular name is "laughing gas."

EXP. 61.—Fit up apparatus similar to that shown in Fig. 23, but use an 8-ounce bottle, so as not to have a large volume of air for the gas to displace, and arrange a small wash-bottle, nearly full of strong nitric acid, in the path of the gas to absorb any nitric oxide which may pass over. Put an excess of zinc into the bottle, and add a small quantity of water through the thistle funnel to just cover the bottom. Place the bottle in a dish of water to prevent a too rapid rise in temperature, and add dilute nitric acid (1 to 1), a little at a time, to keep up a steady stream of bubbles. Collect two jars of the gas, over warm water preferably. Remove the plate from one of the jars; no change in colour is observed. Plunge a glowing splint into the jar; the splint bursts into flame. Heat a little sulphur in a deflagrating spoon until it shows a small flame, and plunge it into a jar of the gas; the flame disappears. Heat the sulphur until it is burning vigorously, and put it into the jar again; it continues to burn, and with a brighter flame than when burning in the air.

Nitrous oxide supports combustion more vigorously than air does, but the burning body must have a sufficient tempera-

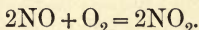
ture to decompose the gas and abstract its oxygen, if the combustion is to continue.

Nitric Oxide, NO , is a colourless gas, which is converted very rapidly into nitric peroxide when mixed with air or oxygen. The gas thus formed has a red colour, so that the change is easily observed, and it is commonly used to distinguish oxygen from nitrous oxide, which does not react with nitric oxide. Thus, the addition of nitric oxide is a test for oxygen, and the addition of oxygen is a test for nitric oxide in mixtures of gases. Nitric oxide is only slightly soluble in water, and does not support the combustion of ordinary burning bodies.

EXP. 62.—Repeat the last experiment, using thin sheet copper in the place of zinc. The bottle need not be cooled, and the wash-bottle must be omitted. Collect two jars of the gas, and remove them from the trough. Collect one tall cylinder about two-thirds full of the gas, and leave it standing over water. Remove the plate from one of the jars; a red gas forms in the mouth of the jar. Plunge a burning candle into the jar: the flame disappears. Just ignite a small piece of phosphorus in a deflagrating spoon and plunge it rapidly into a jar of the gas: the flame disappears. Allow the phosphorus to burn vigorously, and return it to the jar: it burns more vigorously in the nitric oxide than in air. Decant half the volume of oxygen into the jar standing over water: grip the side of the jar in the hand while transferring the oxygen to it. A red gas forms, and dissolves rapidly, the water rising in the jar after each addition of oxygen, and the jar becomes quite warm in the hand.

Nitric oxide, although not a supporter of combustion in the ordinary sense, will give up oxygen to bodies which have a temperature sufficiently high to effect its decomposition.

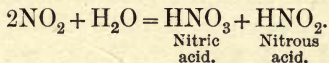
The reaction between nitric oxide and oxygen is expressed by the equation:



Heat is developed by the combination of the two gases.

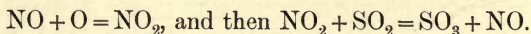
Nitric Peroxide, NO_2 , is a red gas, very soluble in water, with which it reacts, and forms an acid solution containing nitrous and nitric acids. The peroxide itself is not an

acid-forming oxide. The change is expressed by the equation :



The formula NO_2 does not represent the composition of nitric peroxide molecules under all conditions. At a low temperature the composition is more nearly represented by N_2O_4 . If the temperature is allowed to rise, the colour of the gas deepens, and the complex molecules of N_2O_4 are gradually decomposed into the simpler molecules of NO_2 . At a moderately high temperature the composition of the gas is represented by NO_2 . At a still higher temperature the whole of the gas is decomposed into nitric oxide and oxygen, and the colour entirely disappears. As the temperature falls the inverse changes take place. This is a good example of "dissociation."

Nitric peroxide readily gives up part of its oxygen to bodies eager to combine with that element. This is taken advantage of in the manufacture of sulphuric acid, during which nitric oxide is made to act as a carrier of oxygen from the air to sulphur dioxide for its conversion into the trioxide, thus :



These reactions are repeated as long as nitric oxide, sulphur dioxide, and oxygen are present in the acid chambers.

When silver dissolves into nitric acid, both nitric peroxide and nitric oxide are liberated.

The principal reactions of zinc, copper, and silver with nitric acid may be represented by equations :

1. $4\text{Zn} + 10\text{HNO}_3 = 4\text{Zn}(\text{NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}.$
2. $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}.$
3. $4\text{Ag} + 6\text{HNO}_3 = 4\text{AgNO}_3 + 3\text{H}_2\text{O} + \text{NO} + \text{NO}_2.$

The nitrate of the metal is formed in each case.

It is usually stated that hydrogen gas cannot be obtained

by the action of a metal on nitric acid; but if magnesium is substituted for zinc in Exp. 61, the bottle kept cool, and the acid dilute, the greater part of the evolved gas is found to be hydrogen. But if the acid is too strong, and the temperature is allowed to rise, the proportion of hydrogen in the evolved gas is considerably diminished.

EFFECTS OF DILUTION AND TEMPERATURE.

The effects of a variation in the strength of nitric acid, and in the temperature at which the reaction takes place on the volume of the escaping gas, are interesting, and instructive

experiments may be made with the apparatus shown in Fig. 25. A is a test-tube fitted with a bung and angle-tube. B is a small tap funnel. C is a fixed delivery-tube connected with the angle-tube from A by a piece of sound rubber tube, and passing

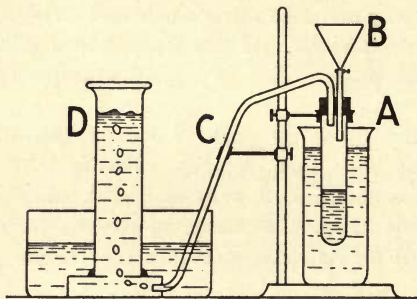


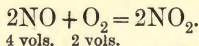
FIG. 25.

under the mouth of the graduated cylinder D. If it is desired to keep the test-tube A cool during an experiment, it is immersed in a beaker containing cold water; or, when the beaker is away, the test-tube can be heated by a Bunsen flame.

The conduct of an experiment is simple. When the parts of the apparatus are in position, water is poured into B and the tap opened. The water running from B into A displaces the air in A and the delivery-tube connected with it. The displaced air collects in D, and its volume can be measured. Thus the volume of air in the apparatus at the beginning of an experiment is known, if the volume of the added acid is

subtracted from the total volume obtained as above. The water is then emptied out, and the necessary quantity of acid added to A ; the coil of weighed metal is dropped in, and the bung quickly replaced. If the tube is to be kept cool, the beaker of water is placed in position. When the metal is completely dissolved, water is poured into B, the tap opened, and the whole of the gas driven from A to D. The volume of gas in D is then measured by depressing the cylinder in the trough until the level of the water is the same inside and outside, and then taking the reading on the graduated scale. Half the volume of oxygen is then passed into D by decanting the gas from a graduated cylinder. When the red gas formed by the reaction between the nitric oxide and oxygen is all dissolved, and the residue is colourless, the cylinder is depressed, and the volume of the residual gas measured. Sufficient data are thus obtained for roughly finding the composition of the evolved gas.

When copper is the dissolving metal, nitric oxide, NO, is the principal constituent of the liberated gas. Now, it has been shown already that when this gas is mixed with oxygen the red gas, nitrogen peroxide, NO₂, is formed and it is easily proved that nitric oxide combines with exactly half its own volume of oxygen during the change. The reaction is shown by the equation :



In the experiments made to obtain the following results, strips of thin sheet copper of uniform size, weighing exactly 1 gram, were used, together with 15 c.c. of the acid. In this way the volume of air in the apparatus was kept the same in each experiment. Now, it must be borne in mind that one-fifth of the enclosed air is oxygen, which will combine with twice its own volume of nitric oxide.

EXAMPLE.—Volume of air in the apparatus after adding the acid=50 c.c. Total volume of gas in D after dissolution of the metal, and displacement of gas in the apparatus by water run in

from B=158 c.c.; volume of oxygen added=80 c.c.; volume of residual gas in D=76 c.c.

Then $158 + 80 - 76 = 162 =$ the volume of NO and O_2 , which has disappeared, and, since two-thirds of this is NO $\frac{162 \times 2}{3} = 108 =$ the volume of nitric oxide in the collected gas.

But 20 c.c. of NO are also accounted for by the 10 c.c. of oxygen in the enclosed air at the beginning of the experiment. Therefore, the total volume of NO liberated = 128 c.c.

Also the residual gas contains 40 c.c. of nitrogen from the enclosed air, and 26 c.c. of added oxygen. Therefore, $76 - 40 - 26 = 10$ c.c. of gas other than nitric oxide liberated from the acid.

Therefore, the NO in the liberated gas = $\frac{128 \times 100}{138} = 92.7$ per cent.

The following table shows the results of two experiments conducted as described above. It demonstrates clearly that the volume and nature of the gas liberated during the reaction between nitric acid and a particular metal depends upon the conditions under which the reaction takes place. One gram of copper was used for each experiment.

It may be remarked that nitric oxide is soluble in the nitric acid solution, and that its solubility decreases as the temperature increases. This would account largely for the difference in the volumes of the gases liberated during the two experiments. The changes taking place between nitric acid and metals deserve more attention than they have yet received; but the subject is a difficult one, and the experiments described above only give a rough indication of the method.

| STRENGTH OF ACID. | | VOLUME OF GAS. | VOLUME OF OXYGEN ADDED. | VOLUME OF RESIDUAL GAS. | PERCENTAGE OF NITRIC OXIDE. | TEMPERATURE. |
|-------------------|--------|----------------|-------------------------|-------------------------|-----------------------------|-----------------|
| ACID. | WATER. | | | | | |
| 1 | 1 | 158 c.c. | 80 c.c. | 76 c.c. | 92.7 | Allowed to rise |
| 1 | 1 | 106 „ | 52 „ | 84 „ | 77.5 | Kept constant |

ACTION OF ACIDS UPON COMMERCIAL IRON.

The different varieties of commercial iron—known as cast iron, steel, and wrought iron—owe their variations in properties very largely to the presence of carbon in the metal. This element may be present, not only in varying proportions, but also in different conditions, and thus cause a wide variation in the properties of the metal.

For our present purpose carbon may be said to exist in iron in two distinct forms. As **Graphite** it is mechanically mixed in the form of crystalline scales with the particles of the iron. These scales are readily seen on looking at the fractured surface of a piece of grey pig-iron with a pocket lens. As **Carbide** it is combined with part of the iron in the form of iron carbide, Fe_3C , which cannot be observed without special preparation of the surface of the metal, and its examination under the microscope.

Cast iron contains on the average 3·5 per cent. of carbon, which exists largely as graphite in grey iron, largely as carbide in white iron, or in both forms in mottled iron. The amount of carbon in **steel** varies considerably, and may be as high as 1·8 per cent. When the steel is in its normal or annealed state, the carbon is in the form of carbide. **Wrought iron** may contain up to 0·2 per cent. of carbon, which is present as carbide. On account of these variations the common acids, though able to dissolve the metal readily, give different results with different varieties.

Hydrochloric and dilute sulphuric acids act similarly, but the action varies with the condition of the carbon. The rate of dissolution increases with the temperature. **Graphite** separates as such, and being insoluble in the acid liquid, settles out, and forms a black deposit on the bottom of the vessel in which the dissolution is taking place. The **carbide** is decomposed by the acid, assisted by the newly liberated hydrogen, and the freed carbon combining with hydrogen forms hydrocarbons, which mix with the escaping gas, and give to it a

very disagreeable odour. The presence of carbide carbon is detected in this way.

Dilute nitric acid acts differently as regards the carbide carbon, which in this case passes into the solution in combination with oxygen and hydrogen. The compound formed imparts a distinct colour to the solution. Under similar conditions the depth of the colour varies with the proportion of carbon present. Graphite, however, is set free, and separates out in the same way as with the other acids.

The other elements present in commercial iron are silicon, phosphorus, sulphur, and manganese, and the purity of the metal depends upon the proportions present, which may vary from traces to several per cents. Each one has its own particular influence upon the properties of the metal, and has to be reckoned with by the practical man. During the dissolution of the metal in acids they undergo various changes. The silicon is oxidized to silica and left as a solid residue, intermixed with any graphite that may be present. Phosphorus and sulphur are oxidized to phosphoric and sulphuric acids by moderately strong nitric acid, and pass into solution. With hydrochloric and sulphuric acids the sulphur escapes entirely as sulphuretted hydrogen gas, and the phosphorus partially as phosphoretted hydrogen. The iron and any manganese which may be present dissolve in and form salts of the acids used.

ACTION OF ACIDS ON METALLIC ALLOYS.

Alloys are bodies containing two or more metals, which may be present under different conditions. Sometimes the relation between them is so intimate that the alloy may be regarded as a chemical compound. Sometimes the body is simply a solidified solution of its constituent metals.

As a rule, neither hydrochloric nor dilute sulphuric acid will dissolve these bodies, and the more intimate the relation between their constituents, the more difficult they are to dissolve. Dilute nitric acid is the best general solvent, and is commonly used. If both metals in an alloy dissolve indi-

vidually in the acid, then the alloy is also soluble ; but if one of the metals is insoluble, it is left as a residue of oxide or metal, as the case may be. A copper-zinc alloy (brass) is completely dissolved. A copper-tin alloy (bronze) is partially dissolved, and a residue of white tin oxide is obtained. A gold-silver alloy containing more than $2\frac{1}{2}$ parts of silver to 1 part of gold is partially dissolved, and a residue of metallic gold left.

The last two reactions furnish the means of separating tin from copper, and gold from silver.

EXP. 63.—Put about 1 gram each of brass and bronze into separate test-tubes ; add 10 c.c. of dilute nitric acid to each, and heat the tube, if necessary, until all action ceases. Repeat the experiment, using dilute sulphuric and hydrochloric acids in place of the nitric acid.

When brass dissolves, copper and zinc nitrates are formed ; and the partial dissolution of bronze results in the formation of copper nitrate and hydrated tin oxide.

ELECTRO-CHEMICAL ACTION.

An important result of the dissolution of a metal in an acid has now to be considered. It has already been noticed that when the action is brisk, the vessel in which it is taking place gets quite hot. It may, then, be said that heat is one of the products of the chemical change ; and under ordinary circumstances, the amount of heat evolved is just as definite as the volume of gas liberated, or the weight of salt formed. This is easy to prove with suitable apparatus, but it is outside ordinary elementary work, and must, therefore, be here taken for granted.

Pure zinc is scarcely attacked by cold dilute sulphuric acid, but if a piece of copper is placed in contact with the zinc in the dilute acid, the action begins, and gas is liberated from the surface of the copper. It would thus appear at first sight as though the copper were dissolving, but it soon becomes evident that this is not so. The solution remains colourless,

which would not be the case if copper sulphate were being formed. Also, the zinc gradually disappears, but the copper, if weighed before being put in, and weighed again after being taken out of the solution, is found to be unchanged. Clearly, then, the contact of the copper with the zinc causes the latter to dissolve more readily, but does not otherwise affect the chemical change. And the solution gets hot, too, so that heat is evolved as usual.

If ordinary sheet zinc is attacked by the dilute acid, it should be cleaned by dipping it in moderately strong acid, and then coated with mercury. Zinc so treated is said to be amalgamated, and acts with the dilute acid in the same way as the pure metal. Silver, platinum, or gas-carbon may be used in the place of copper, to set up the action.

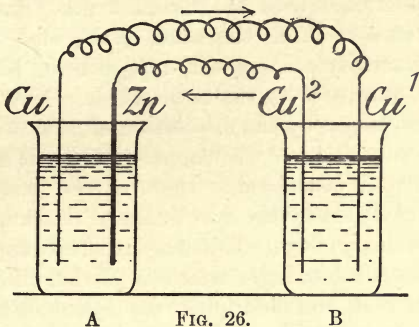
Exp. 64.—Put a piece of pure zinc or the amalgamated metal into a test-tube. Add a few cubic centimetres of dilute sulphuric acid (1 to 20), and allow the tube to stand for a minute or two. Note that no action is going on. Drop a piece of sheet copper on to the zinc. The action commences at once, and soon bubbles of gas are freely liberated from the copper. The solution does not change colour, and the zinc gradually dissolves.

A silver coin, a piece of platinum foil, or a carbon rod may be substituted for the copper with similar results.

If long strips of copper and zinc are only partly immersed in the acid liquid, and the ends outside are made to touch, the same result is obtained. Zinc dissolves, and hydrogen gas is liberated from the copper, even though the immersed portions are some distance apart. Also the ends of the plates may be joined by a metal wire of considerable length with similar results. But directly the connection is severed the action ceases.

Exp. 65.—Cut strips of thick sheet zinc and sheet copper, about 6 inches long by 1 inch wide; immerse the zinc strip about three-quarters the way up in moderately strong sulphuric acid for a few seconds, and then rub a little mercury all over the cleansed surface on both sides. Fix the plates, one on each side of a strip of wood 1 inch wide, so that their ends project a little above the upper surface of the wood. This is easily done by driving short tacks

through the plates into the wood, but not in the same line, so that there will be no danger of their meeting in the wood. Put the plates into a beaker containing dilute sulphuric acid, which should nearly cover the amalgamated part of the zinc plate. Connect the plates by forcing the clean ends of a copper wire between the plates and the wood. Observe that the action commences as soon as the connection is made. Make a similar pair, but with two copper plates instead of copper and zinc. Put this pair into a solution of copper sulphate, and connect the ends by copper wires, as shown in Fig. 26. Allow the action to go on for a few minutes; then take out the copper plates, and examine them.



The copper sulphate solution makes the connection, and the action goes on in A in much the same way as when the connection is made direct by a single wire. The copper plate in B, which is connected directly with the zinc plate in A, is found to be coated with freshly deposited copper, and the longer the action is allowed to proceed, the thicker the deposit becomes. In fact, if the two plates are separately weighed before and after immersion in B, one is found to increase and the other to decrease in weight to exactly the same extent. If the connections are reversed, copper is deposited on the other plate. Evidently some kind of influence is transferred from A to B, which carries the copper from one plate to the other, and its direction depends upon the way in which the connection is made. It seems to move from Cu in A to Cu^1 in B, across the solution to Cu^2 , and back to Zn in A. This is called an **electric current**.

If two or three cells similar to A have their alternate copper and zinc plates connected by short thick copper wires, and

the terminal copper and zinc are connected with carbon rods or platinum plates in B, copper is still deposited on the plate connected with the terminal *Zn*. But in this case nothing dissolves from the other plate, and the copper sulphate is gradually decomposed, oxygen being liberated from the plate connected with the terminal *Cu*. Now, if the amount of heat developed by the dissolution of zinc in the cell during the decomposition of the copper sulphate is determined, it is found to fall considerably short of the quantity which would be developed by the dissolution of the same weight of zinc in the ordinary way. The missing heat appears in the form of electrical energy, which is carried round the system by the current, and determines the decomposition of the sulphate.

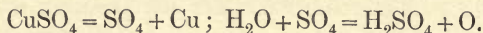
If a very long thin iron wire is used to connect the two plates in A (Fig. 26), nearly the whole of the energy developed by the dissolution of the zinc is transferred to the wire. It appears first as electrical energy, is then carried through the wire by the current, and finally transformed into heat by the resistance of the wire to the passage of the current. With a short thick copper wire for connections, nearly the whole of the heat appears in A.

The principle demonstrated in the last experiment is the one upon which the electro-deposition of metals depends, and it is put to a variety of uses. A large number of metals can be so deposited, and it is only necessary that the surface upon which the deposit takes place should be a conductor of electricity. The common plan is to deposit a metal which has specific properties, such as gold and silver, on account of their lustre, and nickel in virtue of its hardness. It is even possible to deposit two metals together, so as to form an alloy. Thus the deposition of copper and zinc to form a deposit of brass is common. The purification of metals by the use of electrical energy is carried out on the large scale. Electrolytic copper is a very pure metal, which is refined by this process, and is largely used for electrical purposes, and for making high-class copper alloys.

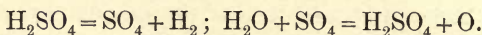
Electrolysis is the term used to denote the process through which a metallic salt or oxide passes when it is decomposed by an electric current. The body undergoing the change is usually dissolved in water; but some solids which can be melted without undergoing rapid decomposition are electrolyzed in the molten condition. The decomposing compound is called the **electrolyte**, and the facts of electrolysis point strongly to a decomposition of at least some of the molecules of the compound by its dissolution in the solvent liquid alone. These molecules, however, are only dissociated, for if the solvent is removed by evaporation the original compound is recovered intact. According to this, when copper sulphate is the electrolyte it seems that an appreciable number of its molecules are dissociated into Cu and SO_4 . The Cu represents an elementary atom or simple radicle, and the SO_4 a group of atoms or a compound radicle, which appears to have properties similar to those of an elementary atom. It must be clearly understood that these radicles are not supposed to exist separately in the same way as an ordinary element or compound. The existence of the one predicates the co-existence of the other in the solution of the salt. They are known as **ions**, and the function of the current is supposed to be to direct them towards the electrodes by which it enters and leaves the solution. The first is the anode, to which the anions move, and the second the cathode, to which the cations move. In the electrolysis of CuSO_4 , the SO_4 groups are the anions and the Cu atoms the cations. When copper electrodes are used the Cu ions simply deposit on the cathode, and lose their ionic condition, while the SO_4 ions deposit on the anode and lose their ionic condition by abstracting copper from the plate itself. But when platinum electrodes are used the SO_4 ions attack water molecules in the proximity of the anode, form H_2SO_4 molecules, and set oxygen free, which collects on the anode plate. The change with the copper anode is in effect a transport of copper from one electrode to the other; with the platinum anode it is equivalent to the

decomposition of copper oxide into its elements. Much more electrical energy is absorbed in the second case than in the first; it is used up in effecting the chemical change in the electrolyte.

This is shown by the equations :



The decomposition of water by the current (p. 27) when regarded from this point of view, is really effected by the electrolysis of a solution of sulphuric acid :



This is supported by the fact that pure water will not convey the current.

The chief electrolytes are solutions of mineral acids and metallic salts, molten salts and oxides, or solutions of oxides in molten salts.

Voltaic Battery.—The simple cell described in Exp. 65 falls off in strength very rapidly, owing to the accumulation of a film of hydrogen on the copper plate. This offers considerable resistance to the passage of the current through the cell, and also sets up a back pressure which diminishes the main current. This is avoided in some constant cells by oxidizing the hydrogen to water, and thus preventing its deposition on the plate. The Bunsen cell is made up as follows: A circular earthenware vessel containing dilute sulphuric acid, in which is immersed a sheet of amalgamated zinc bent round into the form of a hollow cylinder; a porous earthenware pot containing strong nitric acid, in which is immersed a carbon rod. The porous pot stands inside the zinc cylinder, and binding screws are attached to the zinc and carbon plates. The liquids soak into the wall of the porous pot from both sides, and a conducting medium extends between the two plates. When the binding screws are joined by a conductor, a much stronger and more constant current than can be obtained by a simple cell passes through the wire. The function of the nitric acid is

to prevent the deposition of hydrogen on the carbon plate, by oxidizing it to water. By linking several of these cells together in series, a current sufficiently powerful for ordinary experiments is obtained.

SUMMARY.

When a metal dissolves in hydrochloric or dilute sulphuric acid, the reaction is simple, for hydrogen only is liberated, and a salt of the metal and acid formed. The volume of hydrogen set free depends upon the weight of the metal used, and is different for the same weight of different metals. With hot strong sulphuric acid the reaction is more complex, and sulphur dioxide is the principal gas liberated.

Nitric acid dissolves most of the common metals, and gives some very complicated reactions. The products of its decomposition are varied, several oxides of nitrogen, hydrogen, ammonia, and nitrogen itself being liberated under different conditions. The nitrates of the metals are formed in most cases, but with tin and antimony the oxides of the metals are produced. The nitrates are readily decomposed by heat, and, except in one or two cases, a residue of the oxides is obtained.

The experiments on the oxidation of metals in air (Chap. II.) and by nitric acid give interesting comparative results. If a fixed weight of oxygen is taken, and the weights of different metals which would combine with this fixed weight are calculated from the results of experiments, an interesting table can be constructed, as follows :

Combining weight of oxygen = 8.

| METAL. | PARTS BY WEIGHT. | METAL. | PARTS BY WEIGHT. |
|---------------|------------------|-------------|------------------|
| Magnesium ... | 12 0 | Zinc ... | 32·5 |
| Iron ... | 18·7 | Bismuth ... | 69·0 |
| Tin ... | 30·0 | Mercury ... | 100·0 |
| Copper ... | 31·5 | Lead ... | 103·5 |

DISSOLUTION OF METALS AND ACIDS.

| METAL. | NITRIC ACID. DILUTE 1 TO 1. | HYDROCHLORIC ACID. ORDINARY STRENGTH. | SULPHURIC ACID. | | REMARKS. |
|--------------|-----------------------------------|---|--|------------------------------|---|
| | | | DILUTE. | CONCENTRATED. | |
| Aluminium | Very little action | Dissolves rapidly | Very little action | Dissolves slowly on heating | Aqua regia is the best solvent. SbCl_5 is formed |
| Antimony... | Oxidizes, and is partly dissolved | Dissolves slowly when the metal is finely divided | No action | Dissolves on heating | |
| Bismuth ... | Dissolves readily | Dissolves slowly on heating | No action | Dissolves on heating | |
| Cobalt ... | Dissolves readily on heating | Dissolves slowly | Dissolves slowly | Dissolves on heating | The reaction with H_2SO_4 is complex. CuSO_4 is the principal compound formed |
| Copper ... | Dissolves readily | Dissolves slowly with access of air | Dissolves slowly with access of air | Dissolves readily on heating | |
| Cadmium ... | Dissolves | Dissolves | Dissolves | Dissolves on heating | |
| Gold ... | No action | No action | No action | No action | Aqua regia dissolves gold readily, forming AuCl_3 Concentrated nitric acid renders iron "passive" |
| Iron ... | Dissolves readily | Dissolves readily on heating | Dissolves readily on heating | Dissolves on heating | |
| Lead ... | Dissolves readily | Very little action | Very little action | Dissolves slowly when heated | |
| Magnesium | Dissolves very rapidly | Dissolves readily even in very dilute acid | Dissolves readily even in very dilute acid | Dissolves on heating | -ous salt formed with excess of metal; -ic salt with excess of acid Concentrated nitric acid renders the metal "passive" Aqua regia is the best solvent. PtCl_4 is formed Silver sulphate only is formed Stannic sulphate, $\text{Sn}(\text{SO}_4)_2$, is formed |
| Mercury ... | Dissolves readily | No action | No action | Dissolves on heating | |
| Nickel ... | Dissolves readily | Very little action | Very little action | Dissolves on heating | |
| Platinum ... | No action | No action | No action | No action | |
| Silver ... | Dissolves readily | No action | No action | Dissolves on heating | |
| Tin ... | Oxidized to an insoluble oxide | Dissolves somewhat slowly | Very little action | Dissolves on heating | |
| Zinc ... | Dissolves readily | Dissolves readily | Dissolves readily | Dissolves on heating | |

NOTE.—Aqua regia is a mixture of 1 part nitric acid and 3 parts hydrochloric acid; it is made as required.

The numbers are readily obtained, for in Exp. 69 :

| | |
|---|--|
| 0.251 gram of oxygen combines with | 1 gram of copper |
| ∴ 1 „ „ would combine with | $\frac{1}{0.251}$ „ „ |
| ∴ 8 grams „ „ „ „ | $\frac{8}{0.251} = 31.8$ grams of copper |

QUESTIONS.

1. Describe an experiment by which the volume of hydrogen liberated by the dissolution of 1 gram of iron in hydrochloric acid can be determined.

2. What changes take place (*a*) when zinc dissolves in dilute sulphuric acid ; (*b*) when copper and the strong acid are heated together ?

3. How would you find the weight of magnesium sulphate formed when 0.5 gram of the metal dissolves in dilute sulphuric acid ?

4. Give a short description of the general reactions between metals and nitric acid.

5. Name the three common oxides of nitrogen, and briefly describe them.

6. What are the general effects of dilution and temperature on the changes taking place between nitric acid and a given metal ?

7. Which common acid is the best general solvent for metals and alloys, and why ?

8. Describe a simple voltaic cell, and say how you would obtain an electric current with it.

9. What do you understand by the term “electrolysis” ? Give an example to illustrate your answer.

CHAPTER VIII

CHEMICAL EQUIVALENTS AND ATOMIC WEIGHTS OF COMMON METALS AND NON-METALS

THE student is now familiar with the fact that elements combine together to form compounds, and is also aware of the very definite character of these compounds, for he has brought about various combinations, and has seen the extraordinary changes effected in the properties of the elements between which these combinations have taken place. Also, in carrying out the experiments on the dissolution of metals in acids, he has been directed to the conclusion that there is a definite relation between the weight of metal dissolved and the volume of gas liberated during its dissolution. It is also fully recognised that the weight of a given body of gas is just as definite as its volume. This is assumed in Chap. VII., together with the known weight of a litre of hydrogen, which is used to calculate the weights of the volumes of gas evolved in the experiments described ; but it is possible to use a more direct method, if the pure gas only is allowed to escape from the apparatus, and the loss in weight due to this escape is noted.

The object of the following experiments is to make it clear that certain proportional numbers or weights are inseparably associated with the elements when they are entering into combination with each other, or are being expelled from their compounds ; and that these numbers, which are the results of actual experiments, are connected in a simple way with the atomic weights of the elements to which they refer. The

results we obtain may be only approximate ; but if they are sufficiently accurate to give a clear idea of the facts they are intended to illustrate, their object will be attained. Experiments carried out by experienced workers using accurate apparatus fully justify the deductions drawn from them, which may therefore be accepted with confidence.

TO FIND THE WEIGHT OF HYDROGEN EXPELLED FROM AN ACID BY A KNOWN WEIGHT OF MAGNESIUM.

EXP. 66.—Fit up the apparatus shown in Fig. 27. A is a 100 c.c. flask fitted with a two-hole bung. A straight tube, B, fitted with a cap to make it air-tight, passes through one hole, and a bent tube, C, through the other. The other end of C passes through a bung in the U-tube, D. The bend of the U-tube is filled with glass-wool, and each limb with small pieces of fused calcium chloride, and glass-wool on the top. The free limb of the U-tube is fitted with a bung and capped tube. The actual apparatus should weigh about 70 grams. The caps are easily made by pushing short pieces of glass rod into pieces of rubber tube about twice their length.

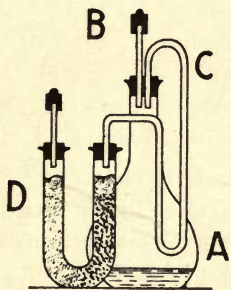


FIG. 27.

Add 10 c.c. of dilute H_2SO_4 (1 in 12) to the flask A, wipe the apparatus, and let it stand for a time near the balance. Weigh accurately about 0.2 gram of Mg ribbon, and make it into a coil, which will pass readily down the neck of A, and stand just

clear of the bung when dropped in. Put the apparatus and weighed magnesium on the scale-pan, and weigh them together. Remove the cap from the tube D. Take the bung out of A, drop in the metal coil, and quickly replace the bung. As the metal dissolves the coil gradually descends until complete dissolution is effected. By this arrangement the evolution of gas is rendered uniform and not too rapid.

Place the apparatus near the balance until it is nearly cold, and then slowly aspirate about a litre of dry air through it. The air is dried by passing through a U-shaped tube fitted in the same manner as D, and attached to B by a rubber tube. Replace the caps, and reweigh the apparatus. The loss in weight is due to the escape of dry hydrogen.

The aspiration of air through the apparatus is of consider-

able importance, as a large portion of the liberated hydrogen remains in the apparatus when the dissolution is finished. Any form of aspirator may be used. In Fig. 28 the inlet of the flask is connected with the drying-tube B, and the outlet of the drying-tube, through which the gas escapes, with the

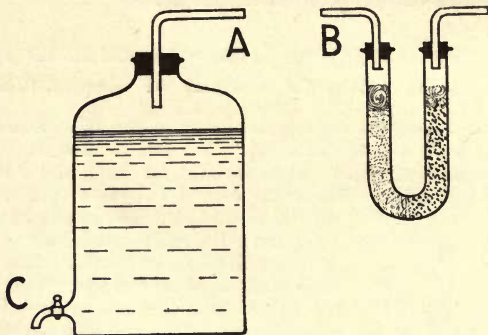


FIG. 28.

aspirator A. The tap C is opened carefully, and about 1 litre of water allowed to slowly escape. The hydrogen is thus replaced by air, and the atmosphere in the apparatus is now similar to what it was at the beginning of the experiment.

| | |
|------------------------------------|-----------------|
| EXAMPLE.—Weight of magnesium taken | = 0.201 gram. |
| „ „ apparatus + magnesium | = 79.296 grams. |
| „ „ „ - hydrogen | = 79.279 „ |
| „ „ hydrogen liberated | = 0.017 gram. |

Simplify this result by calculating the weight of magnesium required to liberate 1 part by weight of hydrogen :

0.017 gram of hydrogen is replaced by 0.201 of magnesium.

$$\therefore 1 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{0.201}{0.017} = 11.82.$$

Or, 11.82 parts of magnesium are equivalent to 1 part of hydrogen.

TO FIND THE WEIGHT OF HYDROGEN EXPELLED FROM AN ACID BY A KNOWN WEIGHT OF ZINC.

EXP. 67.—Repeat the last experiment with about 0.75 gram of thin zinc-foil and 10 c.c. of dilute sulphuric acid (1 in 6). The stronger acid is recommended, as the action is not so violent as with the magnesium.

| | | |
|-------------------------------|---|--------------------|
| EXAMPLE.—Weight of zinc taken | = | 0.743 gram. |
| „ „ apparatus + zinc | = | 77.688 grams. |
| „ „ „ —hydrogen | = | 77.665 „ |
| „ „ hydrogen liberated | = | <u>0.023 gram.</u> |

Then, as before :

0.023 gram of hydrogen is replaced by 0.743 of zinc.

$$\therefore 1 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{0.743}{0.023} = 32.3 \text{ of zinc.}$$

Or, 32.3 parts of zinc are equivalent to 1 part of hydrogen.

These results may be used as starting-points in the determination of the equivalent weights of other elements.

TO FIND THE WEIGHT OF OXYGEN WHICH WILL COMBINE WITH A KNOWN WEIGHT OF MAGNESIUM.

EXP. 68.—Heat a large porcelain crucible and lid (No. 2) over the Bunsen flame, and set it aside to cool. Take a piece of magnesium ribbon 18 inches long and weighing about 0.25 gram; coil it round a piece of thin glass rod, and cut the long coil into six short ones. Weigh the crucible and lid, put in the coils, and weigh again. Put the crucible over a good Bunsen flame on a pipeclay triangle, and slope the lid a little so as to give a narrow air space on one side. Heat the crucible strongly for fifteen minutes without raising the lid. Then raise the lid carefully, and notice if there are any signs of burning. If not, remove the flame, and break up the residue with a clean glass rod, being careful to brush back into the crucible any particles which may adhere to the rod. Continue the heating without the lid for fifteen minutes longer. Allow the crucible to cool, and weigh it. To be quite certain that the action is finished, the crucible should be heated again for a few minutes, cooled, and reweighed to see if the weight is constant.

| | | | |
|---|---|-----------------|-----------------|
| EXAMPLE.—Weight of crucible + magnesium | | | = 33.789 grams. |
| “ | “ | | = 33.544 “ |
| “ | “ | | = 0.245 gram. |
| “ | “ | “ after heating | = 33.951 grams. |
| “ | “ | “ before “ | 33.789 “ |
| Increase | | | = 0.162 gram. |

The increase is due to oxygen absorbed from the air. Take 12 the nearest whole number to the equivalent value found for magnesium, and find the combining number for oxygen :

0.245 gram of magnesium combines with 0.162 of oxygen.

$$\begin{array}{rcl} \therefore 1 & \text{“} & \text{“} & \text{“} & \frac{0.162}{0.245} & \text{“} \\ \therefore 12 & \text{“} & \text{“} & , & \frac{0.162 \times 12}{0.245} & = 7.93 \text{ grams.} \end{array}$$

Then 8 may be taken for the combining proportion of oxygen.

TO FIND THE WEIGHT OF COPPER WHICH WILL COMBINE WITH A GIVEN WEIGHT OF OXYGEN.

EXP. 69.—Heat a No. 1 porcelain crucible over the Bunsen flame. Allow it to cool; weigh it, and weigh in it 1 gram of finely-divided copper reduced from the oxide. Put the crucible in a fire-clay dish, and place the dish in a moderately hot muffle. Continue the heating for forty-five minutes; remove the crucible; cool, and weigh it. Repeat the heating for ten minutes, and reweigh to see if the weight is constant.

| | | | |
|--|---|------------|---------|
| EXAMPLE.—Weight of crucible + copper after heating | | | Grams. |
| “ | “ | “ before “ | 12.851 |
| “ | “ | “ before “ | 12.600 |
| Increase | | | = 0.251 |

Weight of copper taken = 1 gram.

Now, 0.251 gram of oxygen combines with 1 gram of copper ;

$$\therefore 8 \text{ grams of oxygen combine with } \frac{8}{0.251} = 31.88 \text{ of copper.}$$

31.5 may be taken as the combining proportion of copper.

NOTE.—The reduced copper for the experiment is readily prepared by reducing powdered copper scale by coal gas or hydrogen. The common commercial oxide is too impure to give a good result.

TO FIND THE WEIGHT OF COPPER EXPELLED FROM ITS COMPOUNDS BY A KNOWN WEIGHT OF ZINC.

EXP. 70.—Dissolve about 3 grams of crystallized copper sulphate, $\text{CuSO}_4, 5\text{H}_2\text{O}$, in 50 c.c. of water ; filter the solution, if necessary, into a small beaker. Weigh accurately about 0.5 gram of thin zinc-foil, and transfer it to the sulphate solution. Heat the solution gently, and stir occasionally with a glass rod until the zinc is completely dissolved. This is determined by breaking up the precipitated copper with the end of the glass rod. While the dissolution is proceeding fold two filter-papers and put them in a filter-funnel in the air-oven, or over the sand-bath, to dry. When dry place one in each pan of the balance, and counterpoise them, cutting the apex off the heavier one and then snipping the one or the other at the top until they counterpoise. Then put the complete filter into the one which has had the apex cut off, and open it out so as to make a single filter with four folds of paper on each side. Put it into the funnel, and when ready filter the sulphate solution. Transfer the whole of the precipitated copper to the filter, and wash it thoroughly until every trace of the excess of copper sulphate has been washed through. Use a wash-bottle in which the water can be heated, as the washing is effected more rapidly with hot than with cold water. Place the filter funnel and filter in a cone over the sand-bath or in the air-oven. Be careful not to overheat the filter, or the finely-divided copper will absorb oxygen, and too high a result will be obtained. When the copper is thoroughly dry, separate the two filters and put them on the scale-pans in the same order as when they were counterpoised ; add weights until they counterpoise again. The difference gives the weight of the copper. Repeat the drying for a few minutes to see if the weight is constant.

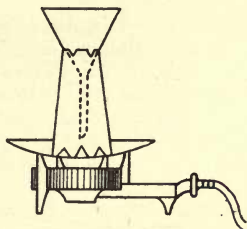


FIG. 29.

By using two filters as described loss of copper is avoided, and by putting them both in the funnel any loss of weight due to washing is the same in both.

TO FIND THE WEIGHT OF CHLORINE WHICH WILL COMBINE WITH A KNOWN WEIGHT OF SILVER.

EXP. 72.—Weigh accurately about 0.5 gram of fine silver; transfer it to a small beaker, and add 5 c.c. of dilute nitric acid (1 to 1); heat the beaker gently on the hot plate until the metal is dissolved; make up the solution to about 100 c.c. with distilled water; raise it to boiling, and add a little dilute hydrochloric acid; stir well with a glass rod until the white curdy precipitate collects together; add a few drops more of the acid to see if the precipitation is complete. Add the acid carefully, so as to have only a slight excess in the solution when the whole of the silver is precipitated. Dry and counterpoise two filter-papers as in Exp. 70. Filter off the silver chloride, and wash it thoroughly with hot water. Dry the chloride carefully, separate the filters, and weigh. Repeat the drying and weighing until a constant weight is obtained.

EXAMPLE.—Weight of silver chloride obtained = 0.675 gram.

| | | | | | |
|---|---|----------------|---|---------------|---|
| “ | “ | “ | “ | taken = 0.509 | “ |
| “ | “ | chlorine found | | = 0.166 | “ |

0.509 gram of silver combines with 0.166 gram of chlorine;

| | | | | | | | | | |
|---|---|---|---|---|---|---|-----------------------|---|---|
| ∴ | 1 | “ | “ | “ | “ | “ | $\frac{0.166}{0.509}$ | “ | “ |
|---|---|---|---|---|---|---|-----------------------|---|---|

| | | | | | | | |
|---|-----------|---|---|---|---|----------------------------------|---------------------------------|
| ∴ | 108 grams | “ | “ | “ | “ | $\frac{0.166 \times 108}{0.509}$ | = { 35.22 grams of chlorine. |
|---|-----------|---|---|---|---|----------------------------------|---------------------------------|

35.5 may be taken as the equivalent of chlorine.

If potassium bromide and potassium iodide solutions are used to precipitate known weights of silver, in the same way as described in the last experiment, the combining proportions of bromine and iodine can be determined as readily as that of chlorine.

If known weights of sodium chloride and potassium bromide are precipitated with excess of silver nitrate, and the precipitates collected and weighed, the combining proportions of sodium and potassium, compared with chlorine and bromine respectively, are obtained.

SUMMARY OF RESULTS.

The experiments by which the results given in the previous examples were obtained were made with special care, so as to furnish reliable standards for the student to work to. Therefore, the beginner must not expect too much from his own initial experiments, and should be satisfied if his results are sufficiently near the true ones to give him confidence in the general principles which are under investigation, and in the results which are stated as the outcome of many most accurate investigations.

It should be borne in mind that if two or more distinct methods are used to determine the chemical equivalent of a particular element, the results should be practically the same. This is illustrated in the determination of the equivalent of copper: (a) by its combination with oxygen; (b) by its precipitation by zinc.

The common starting-point is hydrogen, because it has the lowest equivalent of any known element. It therefore furnishes a very simple standard; but any other element might be used. Berzelius, who was the first to furnish a well-defined list of the equivalents or combining proportions of elements, adopted $O = 100$ for his standard. But it is readily seen that such a standard would be somewhat cumbersome in its application.

The chemical equivalents or combining proportions of elements are *experimental* numbers, and do not depend upon any *theory* of the constitution of compounds, other than that they contain elements in chemical combination. No difficulty would, however, be experienced in assigning symbols to these combining proportions, and in representing compounds with them; but formulæ of compounds derived in this way would not agree in many cases with those found by the application of the theory of atoms. It is therefore necessary to consider the question from another point of view, and endeavour to trace a relation between chemical equivalents and atomic weights.

RELATION OF CHEMICAL EQUIVALENTS TO ATOMIC WEIGHTS.

| ELEMENT. | SYMBOL. | i EQUIVALENT. | ii ATOMIC WEIGHT. | RATIO OF i : ii |
|---------------|---------|------------------|----------------------|-----------------|
| Hydrogen ... | H | 1.0 | 1.0 | 1 |
| Chlorine ... | Cl | 35.22 | 35.5 | 1 |
| Silver ... | Ag | 107.71 | 107.7 | 1 |
| Oxygen ... | O | 7.93 | 16.0 | 2 |
| Magnesium ... | Mg | 11.82 | 24.0 | 2 |
| Copper ... | Cu | 31.47 | 63.0 | 2 |
| Zinc ... | Zn | 32.3 | 65.0 | 2 |
| Bismuth ... | Bi | 69.21 | 207.5 | 3 |
| Tin* ... | Sn | 29.4 | 117.4 | 4 |

Atomic Weights.—Certain numbers, termed atomic weights, have been used in connection with elements in preceding chapters, and a reference to the table given above indicates that the *combining proportion* of an element as determined by experiment does not always agree with its *atomic weight* as commonly used. Although the relation between the two is a simple one, it requires some explanation if the beginner is to use atomic weights with the confidence they deserve. It may be stated that the determination of the combining proportion of an element is always the first step in the fixing of its atomic weight, and that the other considerations are also based on experimental grounds. What these considerations are depends upon the nature of the element and its compounds; so that a method which is very useful in dealing with some elements may entirely fail with others. Often two or more methods may be applied to the same element, and if their results agree, the deductions drawn from them are all the more convincing. The method of deducing an atomic weight may depend upon either the properties of the element itself or on those of its compounds. The important methods used for fixing the atomic weights of elements when their combining proportions are known will now be briefly, but sufficiently, described, to enable the student to get a general grasp of the

* See Exp. 56.

subject ; but for fuller details larger works on chemistry must be consulted.

Vapour Density.—A number of elements and compounds are either gaseous at the temperature of the atmosphere, or are converted into gas when raised to temperatures within the range of accurate experimental work. The weights of measured volumes of these gases or vapours can be determined, and compared with the weights of equal volumes of hydrogen. This gives the vapour density of the element or compound in the gaseous state.

There are several methods employed for the determination of vapour density ; but a brief outline of a comparatively simple one will be sufficient for our present purpose. Suppose the compound under consideration to be a liquid which is easily converted into a combustible vapour. A glass flask with its neck drawn off to a narrow tube is weighed, and an excess of the liquid introduced. The flask is then immersed in a bath, the temperature of which is well above the boiling-point of the liquid, when a considerable volume of the vapour escapes and carries with it the air which originally filled the flask. When the air is all expelled, and the liquid is completely converted into vapour, the flask is full of it at the temperature of the bath and the pressure of the outside atmosphere. If the jet of vapour is allowed to burn as it issues from the neck, the end of the vaporization is indicated by a sudden drop in the flame. The end of the neck is now sealed up by softening the glass in the blow-pipe flame, the flask removed from the bath, and weighed when cold. The end of the neck is then broken under water, the flask entirely filled, and weighed again full of water. The weight of the water in grams gives the volume of the flask, for a gram of water measures a cubic centimetre. The weights obtained, together with the corrections to reduce the volume of the vapour at the temperature and pressure of the experiment to its volume at N.T.P. (see Appendix), and for the expansion of the flask,

give the weight and volume of the vapour under examination. It is then easy to compare this weight with the weight of an equal volume of hydrogen under the same conditions of temperature and pressure. It may, then, be stated that the vapour density of an element or a compound which can be converted into vapour without decomposition or dissociation is an experimental number ; and full advantage may be taken of the fact in helping to fix atomic weights.

If it is assumed that the bulk of 1 part by weight of hydrogen represents the volume of an atom of the element, it may be chosen as the unit of comparison for other atomic and molecular volumes. Twice this bulk of hydrogen represents a molecule of the gas, and, by Avogadro's law (see p. 43), any other molecule in the gaseous state fills the same volume. From the definition of the term atom, a molecule of any kind cannot contain less than an atom of an element.

So that the smallest weight of an element ever found in a molecular volume of the vapour of any of its compounds may be taken as the atomic weight of that element.

Further, it appears that vapour densities furnish a direct method of determining molecular weights ; for since it is assumed that a molecule of hydrogen contains two atoms, its weight is twice that of a single atom, so that the weight of a molecule of any other gas must be proportional to twice its vapour density. If, then, the atomic weights of the elements in a compound are known, and its vapour density can be determined, a definite molecular weight is readily assigned to it. For example, the smallest weight of oxygen ever found in two volumes of any of its volatile compounds is 16 ; the vapour density of water is 9 ; and, therefore, its molecular weight is 18 ; so that a molecule of water contains an atomic weight of oxygen, and 2 atomic weights of hydrogen and its formula is therefore H_2O .

The majority of the metals cannot be vapourized at workable

temperatures, nor do they furnish volatile compounds, so that the application of the above principle to the fixing of their atomic weights is limited. The problem must in their case be solved by other means, as described below.

Isomorphism.—Metals can be arranged more or less definitely into groups, such that the members of any one group can replace each other in solid compounds without altering the crystalline form of the compounds. These metals and their crystallized compounds are said to be isomorphous, and their atoms are regarded as fulfilling similar functions in the molecules of the compounds. If, then, the atomic weight of one metal in a group has been fixed by any other method, the atomic weights of the other members of the same group can be deduced. Thus the chemical equivalent of aluminium is 9, and it forms only one oxide, in which the proportion $\text{Al} : \text{O}$ is $18 : 16$; if it is inferred that the formula of this oxide is AlO , the atomic weight of the metal must be taken $\text{Al} = 18$. But from other considerations the formula of the red oxide of iron is given as Fe_2O_3 , and the oxide of aluminium is isomorphous with it, so that the more probable formula is Al_2O_3 , and in this case the atomic weight of the metal is $\text{Al} = 27$. (See also "Double Salts and Isomorphism" in Chap. IX.)

Atomic Heat.—The quantity of heat which a given weight of a metal absorbs while its temperature rises through a given range, is defined as the specific heat of the metal. The quantity of heat required to raise the same weight of water through the same range of temperature is taken as the unit. Now, it is found that the quantity of heat absorbed by a solid metal is inversely proportional to its atomic weight. Or, if weights of several metals proportional to their atomic weights are taken, the same quantity of heat is required to raise each of these weights through the same temperature. From this it appears that the specific heat of a metal multiplied by its atomic weight furnishes a quantity which is the same for all metals. 6.2 is a mean value for this quantity, which may be

defined as the atomic heat of the metals, or as the specific heat of their atomic weights. This is summarized in the equation :

$$\begin{array}{rcl} \text{Specific heat} \times \text{atomic weight} & = & 6.2 \\ \text{Therefore atomic weight} & = & \frac{6.2}{\text{Specific heat}} \end{array}$$

Thus, when the specific heat of a metal has been determined, this principle, which is known as the law of Dulong and Petit, must afford considerable help in fixing its atomic weight.

The solid non-metals are usually included in the general statement, but for carbon, boron, and silicon the atomic heat is abnormal, and varies for the different allotropic modifications of these elements. If, however, their specific heats are determined at high temperatures, when their molecules probably have a simpler structure, a much closer approximation to the mean atomic value is obtained. So that the principle may probably be said to include all solid elements.

Chemical Considerations.—The formula for water was at first written HO , and is correct in so far as it represents the equivalent weights of the two elements in the compound—*i.e.*, 1 : 8. But do these symbols represent atoms according to the present view of the atomic hypothesis? One of the first principles of the atomic theory is that when a chemical change takes place in the properties of a substance, it is the individual molecules which undergo the change, and this is true for both elements and compounds. In Exp. 16 it is proved that when sodium acts upon water, hydrogen gas is liberated. Where does this hydrogen come from? From the molecules of the water is the only satisfactory explanation. Now, it is found that water disappears in the same proportion as hydrogen appears, and, if a given weight of sodium is used, an equivalent weight of hydrogen is obtained. Also, if the residual liquid is evaporated to get rid of the excess of water, a white solid residue is obtained. This is the common

compound known as caustic soda, which, since nothing but hydrogen and excess of water have escaped, must contain the remnants of the water molecules, together with the sodium used to bring about the change. Now, if this solid is heated with more sodium, a further quantity of hydrogen is obtained, and this, too, must come from the remnants of the water molecules associated with the first quantity of the metal. The residue from this change is a solid when cold, and is quite free from hydrogen. From this it appears that hydrogen can be expelled from the water molecules in two distinct portions. Other metals will displace this second proportion of hydrogen from caustic soda, and their action can be more readily controlled.

EXP. 73.—Weigh 2 grams of caustic soda, and put it together with 20 c.c. of water into the flask A (Fig. 21). Add 0.25 gram of aluminium foil, and gently heat the mixture on the hot gauze. Test the gas collected in C. The characteristic explosion of a mixture of air and hydrogen is obtained. Hydrogen is displaced from the caustic soda by the aluminium, and a double oxide of aluminium and sodium is formed.

The inference to be drawn from these experiments is, that since hydrogen can be expelled from the water molecules in two distinct portions, there must be at least two atoms of hydrogen in each molecule of water. No experiment has yet been made in which the gas is displaced in more than two portions.

Further, it is possible to displace oxygen from water, but it all comes out at once. The simple explanation of this is that there is only one atom of oxygen in the water molecule. If, then, symbols are used to represent atoms, there is clearly only one way to write the formula for water—*i.e.*, H_2O . This is also borne out by the results of Exp. 19, by which it is proved that water contains hydrogen and oxygen in the proportion of 2 to 1 by volume. For by Avogadro's law equal volumes of gases under normal conditions contain the same number of molecules. Therefore, the water molecules must

supply double the number of hydrogen atoms to make up the double volume of that gas obtained from the water.

If, then, the formula H_2O is admitted, and the atomic weights are based upon $H=1$ for the standard, it is evident that $O=16$, or the atomic weight of oxygen is double its chemical equivalent.

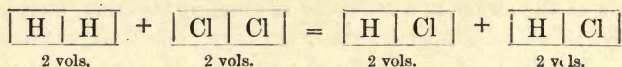
The properties of water are so different from those of its constituents that there must be a very intimate relation between the atoms of oxygen and hydrogen in the molecules of water. Some very powerful influence is at work holding the atoms together, and this must reside in the atoms themselves, for the energy of combination cannot exist apart from the constituents of the compound. It is not difficult, then, to think of the atoms in a molecule as clinging together, merging their individual properties into each other, and thus producing a new particle, with well-defined properties of its own. If this is so, an atom of oxygen must have twice the clinging power of an atom of hydrogen, and this may be shown graphically by writing the formula for water thus, $H-O-H$. Several names have been given to this important property of atoms, and the best are given below.

Atom-combining Power, Valency, and Atomicity.—

When sodium pushes out part of the hydrogen from water, it evidently displaces an atom from each molecule acted upon, and an atom of sodium takes its place. This is shown by writing the formula of caustic soda thus: $Na-O-H$; and it is seen that the *atom-combining* power of sodium is the same as that of hydrogen. This is shown again when the second part of hydrogen is displaced by sodium, and the formula becomes $Na-O-Na$. Again, magnesium or zinc pushes the whole of the hydrogen out of water at one operation, and it is not difficult to conceive that an atom of magnesium or zinc enters each molecule to take the place of the two atoms of hydrogen displaced. Hence the change is from $H-O-H$ to $Mg=O$ or $Zn=O$, and the atom-combining power of these

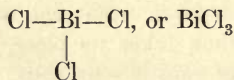
metals is equal to that of oxygen. From this it seems that the term *atom-displacing* power also expresses this property of atoms.

When a mixture of hydrogen and chlorine is fired, rapid combination takes place between the two gases, and they disappear in exactly equal volumes to form hydrochloric acid gas, the total volume of which is the same as that of the disappearing gases. Now, it is practically certain that the molecules of the elementary gases contain two atoms; and by Avogadro's law the equal volumes contain the same number of molecules. Therefore, it may be considered that each pair of hydrogen and chlorine molecules in the mixture divide up and have their atoms rearranged. Thus:

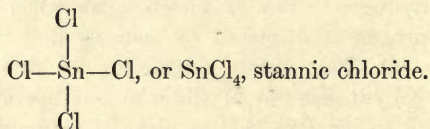


This points to chlorine and hydrogen combining together atom to atom. They have, therefore, the same combining power. This information is useful, as it gives another standard by which to measure the combining power of metals, since they all unite with chlorine, and the relative number of atoms in the molecules of their chlorides can be determined.

Bismuth unites with chlorine and forms a compound, the formula of which may be written graphically, thus:



Tin unites with chlorine to form the compound:



It may be noticed here that tin also unites with two atoms of chlorine to form the compound SnCl_2 , stannous chloride. So that the total combining power of an elementary atom

need not be always used up in the formation of a molecule. But the compound formed is "unsaturated," and can take up a second proportion of the other element to form the higher compound.

Reference to the table on p. 125 will now make it clear that the number which expresses the ratio of the chemical equivalent of an element to its atomic weight, also gives its atom-combining power or valency. This part of the subject should be carefully studied, and not put aside until the principles are quite clear.

Atomic weight and valency are fundamental properties, and are in constant use for determining the formulæ by which compounds are to be represented. Chap. IX. should be studied in conjunction with this one, for a further development of the subject of chemical formulæ. The following table contains the common elements arranged in groups according to their valency, which is indicated by a number attached to the typical element of each group. When an element appears in more than one group it is an indication that its active valency varies in different compounds.

TABLE OF ATOM-COMBINING POWER OR VALENCY OF ELEMENTS.

| MONADS. | DIADS. | | TRIADS. | TETRAIDS. | PENTADS. | HEXADS. |
|-----------|-----------|-----------|------------|-----------|------------|----------|
| H=1. | O=2. | O=2. | N=3. | C=4. | P=5. | S=6. |
| Hydrogen | Oxygen | Magnesium | Nitrogen | Carbon | Phosphorus | Sulphur |
| Chlorine | Carbon | Manganese | Boron | Sulphur | Nitrogen | Chromium |
| Bromine | Sulphur | Mercury | Phosphorus | Silicon | Antimony | Cobalt |
| Iodine | Barium | Nickel | Antimony | Aluminium | Arsenic | Iron |
| Fluorine | Calcium | Platinum | Arsenic | Chromium | Bismuth | Platinum |
| Potassium | Strontium | Iron | Bismuth | Iron | | Tungsten |
| Sodium | Copper | Lead | Gold | Lead | | |
| Silver | Cadmium | Tin | | Platinum | | |
| | Cobalt | Zinc | | Tin | | |
| | Chromium | | | | | |

SUMMARY.

The chemical equivalents of the elements in general, or their quantitative relations to each other, form the solid

foundation upon which all systematic practical work is based. Mere observation is useful for indicating the way, but it is only when one begins to weigh and measure that the great possibilities of the subject become apparent. The selection of hydrogen as the standard weight renders comparison easy. The chemical equivalent of an element is purely the result of experiment, and is quite independent of any theory of the constitution of matter. The atomic weight of an element, on the other hand, assumes the existence of atoms, and is dependent on the atomic theory for its definition; but it is none the less certain on that account, for it is simply the chemical equivalent multiplied by a whole number. The selection of this number for a particular element is also based upon experimental methods, and the number itself indicates the atom-combining power or valency of the element. The great care which has been exercised in the determination of atomic weights renders them perfectly reliable for use in the most important calculations, and every confidence may be placed in them.

QUESTIONS.

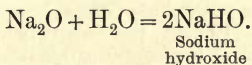
1. What do you understand by the chemical equivalent of an element?
2. Describe two methods by which the chemical equivalent of copper can be determined.
3. What is meant by the valency of an element? Give examples.
4. Describe experiments in which hydrogen is displaced from water in two distinct operations.
5. What is the relation between the chemical equivalent of an element and its atomic weight?
6. Explain the difference between the atom-combining power of an element and its combining weight.

CHAPTER IX

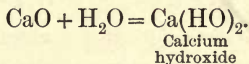
OXIDES, ACIDS, AND SALTS

ALL the metals combine, either directly or indirectly, with oxygen to form oxides; but those oxides which cannot be formed by direct oxidation are unstable bodies of little practical importance. The common metals which do not oxidize, when exposed to air or oxygen under suitable conditions, are silver, gold, and platinum.

A few of the common oxides unite directly with water to form compounds, called **hydroxides** or **hydrates**. These definite bodies contain the elements of the oxides and of water. Thus, sodium oxide, Na_2O , and potassium oxide, K_2O , form very stable compounds with water, which are not decomposed at a bright red heat. This kind of change is readily shown:



Calcium oxide (quicklime), CaO , and the corresponding oxides of barium and strontium, combine readily with water, and a considerable amount of heat is developed during the reaction. Thus:



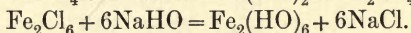
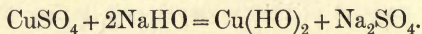
These hydroxides, however, are decomposed at a red heat, and the water escapes, leaving the original oxides as a residue. The change shown in the last equation is then reversed. The evolution of heat is readily observed on moistening a piece of quicklime with water.

Hydroxides which can be formed by the direct union of oxides with water are more or less soluble in the liquid, and their solutions have very characteristic properties. They produce a soapy feeling when rubbed between the thumb and finger, and the very soluble ones have a caustic or burning action upon the skin. They all turn reddened litmus **blue**. This is called an **alkaline** reaction, and the compounds producing it are alkaline hydroxides.

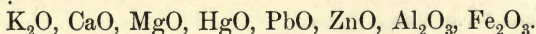
The soapy feeling mentioned above is really due to the formation of a soap, by a reaction between the alkali and the fatty matter in the skin. The common alkalies, caustic soda and caustic potash, are largely used, on account of this property, for the removal of grease from various articles. The soap formed is readily washed away, and the grease thus removed. Hydroxides of metals, the oxides of which do not combine directly with water, can be formed in an indirect way. They are insoluble in water, and when a solution of a soluble hydroxide is added to a solution of a salt of one of these metals, the hydroxide of the metal is generally formed, and precipitated from the solution.

Exp. 74.—Put a crystal of copper sulphate into a test-tube, and dissolve it in a little water; add a solution of caustic soda, a little at a time, as long as a precipitate forms; shake well, and allow the precipitate to settle. Repeat the experiment with a solution of ferric chloride in place of the copper sulphate.

The green and brownish-red precipitates are hydroxides, and the changes are shown by the equations:

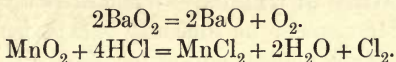


Basic Oxides.—Metallic oxides which form hydroxides, either soluble or insoluble, corresponding to the above, are called **basic oxides**, and it is very probable that, if the insoluble ones could be dissolved in water, their solutions would give an alkaline reaction. The following are examples of basic oxides:



Peroxides.—But some metals form more than one oxide, and it is then necessary to enquire if all the oxides of a particular metal are basic in character.

Compare PbO and PbO_2 ; BaO and BaO_2 ; MnO and MnO_2 . The second oxide in each pair gives off oxygen gas when it is heated alone, or with dilute sulphuric acid; and when heated with hydrochloric acid causes the liberation of chlorine from the acid. For example :



These higher oxides are not true basic compounds, and are usually called peroxides.

Complex Oxides.—Another class of oxides, of which red lead, Pb_3O_4 , and magnetic oxide of iron, Fe_3O_4 , are examples, are sometimes regarded as being a combination of two oxides of the same metal. Compare Pb_3O_4 and 2PbO.PbO_2 ; Fe_3O_4 and $\text{FeO.Fe}_2\text{O}_3$. They are not true basic oxides.

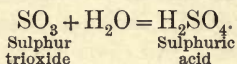
Acid-forming Oxides.—A few metallic oxides are even more highly oxidized than the peroxides. A well-known example of such compounds is the highest oxide of chromium, CrO_3 . This oxide when in solution has distinctly acid properties, and is altogether different from the basic oxides of the same metal. It is an acid-forming oxide.

Metallic oxides may, then, be divided into four classes : (1) basic oxides ; (2) peroxides ; (3) complex oxides ; (4) acid-forming oxides.

Oxides of Non-Metals.—The most powerful acid-forming oxides are to be found among the oxides of the non-metals. They unite with water to form hydroxides, which are mostly soluble in water, and form solutions having very characteristic properties. The solution of an acid hydroxide has a **sour** taste, and turns litmus* **red**. This is the characteristic acid

* Litmus is a vegetable colouring matter. It dissolves readily in water, and either the solution itself or porous paper stained with it may be used for testing.

reaction, as distinguished from the alkaline or basic reaction, in which reddened litmus is turned **blue**. The formation of an acid hydroxide is represented thus :



A few of the non-metals form peroxides, and some of the non-metallic oxides are neutral in character.

Nomenclature of Oxides.—When there is only one oxide of a particular element no difficulty is experienced in giving it a name, as MgO, magnesium oxide ; ZnO, zinc oxide. But, when there are two or more oxides of the same element, distinguishing names must be used. Thus, copper forms two compounds, commonly called the red and black oxides, from their respective colours. The systematic names are **cuprous** oxide, Cu₂O, and **cupric** oxide, CuO. Similarly, we have ferrous and ferric oxides, FeO and Fe₂O₃. The termination **-ous** indicates the oxide containing the smaller proportion, and the termination **-ic** the larger proportion, of oxygen. The prefix **sesqui-** is also used to denote the ratio 2 to 3. Sesquioxide of iron is ferric oxide, Fe₂O₃.

The same terminations are used to distinguish hydroxides of the same element from each other. There are ferrous and ferric hydroxides ; and the two important acid hydroxides of sulphur are **sulphurous** and **sulphuric** acids, H₂SO₃ and H₂SO₄.

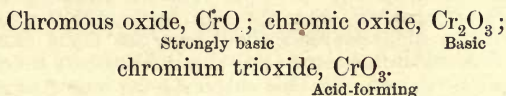
Another useful way of naming is to put a numerical prefix before the word “oxide,” and also before the name of the other element, if necessary. The prefixes indicate the number of atoms of oxygen or of the other element in the formula.

Thus sulphur **dioxide**, SO₂ ; sulphur **trioxide**, SO₃ ; and **triferric tetroxide**, Fe₃O₄. Other examples are carbon **monoxide**, CO ; carbon **dioxide**, CO₂ ; chromium **trioxide**, CrO₃ ; nitrogen **tetroxide**, N₂O₄ ; phosphorus **pentoxide**, P₂O₅.

Acid-forming oxides are often called **anhydrides**, as sulphuric anhydride, SO₃.

Many compounds have common names, with which the student will become familiar, and, with a little practice, he will have no difficulty in giving the systematic name to any compound, when he knows its formula.

Basic and acid-forming oxides are the most important, and it may be stated definitely with regard to their distinctive properties that, if there are two basic oxides of the same metal, the **lower** oxide is the **stronger** base. Thus, FeO is a stronger base than Fe_2O_3 . On the other hand, of two acid-forming oxides of the same element the **higher** oxide forms the **stronger** acid. Thus, sulphuric acid is more powerful than sulphurous acid. With some of the metals, both acid-forming and basic oxides are obtained. This is so with the oxides of chromium :



REACTIONS BETWEEN BASIC OXIDES AND ACIDS.

The acid hydroxides are such well-defined compounds that they were, for a long time, considered to be the typical acids, and the oxygen they contain absolutely essential to the composition of an acid. But when it was conclusively proved that hydrochloric acid contains no oxygen, this view had to be modified. Now, clear proof has been furnished that, when some of the metals are presented to the common acids, they displace hydrogen and take its place, forming **salts** of the acids. So that it would appear that the essential element in an acid is the hydrogen which can be displaced from it by a metal. Now, only a comparatively small number of metals will displace hydrogen from acids in general, but a large number of basic oxides and hydroxides will react with most acids and form salts of the acids used. Thus copper does not dissolve in either dilute sulphuric or hydrochloric acid, but cupric

oxide does dissolve, and forms the copper salts of the acids. Thus :

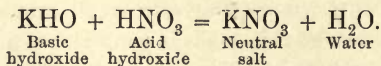
1. $\text{CuO} + 2\text{HCl} = \text{CuCl}_2 + \text{H}_2\text{O}.$
2. $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}.$

It is seen from the equations that the hydrogen of the acid is replaced by the metal of the oxide, and that the displaced hydrogen unites with the oxygen of the oxide to form water. This is the general reaction.

The experiments which follow are intended to make the beginner practically acquainted with the commoner reactions between oxides and acids.

Exp. 75.—Weigh roughly 3 grams of caustic potash, put it into a porcelain basin with 10 c.c. of water, and stir the liquid with a glass rod until the solid is dissolved. Test the solution with a piece of red litmus-paper, and leave the paper sticking to the side of the dish, so that a slight movement will bring the liquid into contact with it. Now add dilute nitric acid (1 to 1) a little at a time, stirring with a glass rod, until the blue colour of the litmus-paper is just turned red when the solution is brought into contact with it. Towards the end the acid must be added drop by drop. The first portion of the acid may be run in from a test-tube, and the remainder from a piece of glass tube pulled off to a jet. The dropping-tube is put into the test-tube containing the acid, and when some of the liquid has entered, the top of the tube is closed by the finger, and the tube itself lifted out. By moving the finger the acid is allowed to escape drop by drop. When the action is finished, remove the litmus-paper, evaporate the solution down to about 15 c.c., and set it aside to crystallize. Examine the crystals, and compare them with the saltpetre crystals in the laboratory bottle.

In this experiment it is clear that the basic properties of the alkali and the acid properties of the acid have entirely disappeared, along with the bodies themselves, and a new body has been formed. The reaction is expressed thus :



This equation not only shows the general change, but also expresses these quantitative relations between the reacting

compounds. These relations are just as definite as those which exist between the elements in an oxide, or between the amount of a dissolved metal and the gas liberated during its dissolution. This is easily proved by using solutions of acids and alkalies containing known weights of the reacting compounds, and finding the volumes of the liquids required to be added together to bring about neutralization.

Solutions containing 10 grams per litre of each of the following pure compounds are easily prepared: sulphuric, nitric, and hydrochloric acids, caustic soda and caustic potash. Directions for the preparation of one of them is given on p. 143, but they should be ready prepared for the student's use.

The following exercises may be made successful with moderate care, and will give a good insight into the quantitative relations which exist during neutralization. Litmus has been used so far as an indicator of the acid or alkaline character of a solution; but, for the work now to be described, **methyl orange*** is to be preferred, as it is not affected by carbon dioxide in solution. It is turned greenish-yellow by an alkali, but changes to a bright red on the addition of a very slight excess of an acid.

EXP. 76.—Wash out the burette (Ch. xv.) with a little of the standard acid solution, fix it in the clip, and fill it up to the mark with the same solution. Transfer 10 c.c. of the caustic soda solution to a conical flask, by means of a 10 c.c. pipette, add about 100 c.c. of water to the flask, and one or two drops of methyl orange. Note the level of the acid solution in the burette, and then run a little at a time into the flask, shaking it between each addition, until the yellow-green colour of the solution changes to red. Care must be exercised towards the end of the reaction, as one drop of the acid solution is sufficient to change the colour. Read off the volume of acid solution added. Repeat the experiment with a second 10 c.c. of the soda solution, and compare the two results.

An exactly similar experiment may then be made with caustic potash solution.

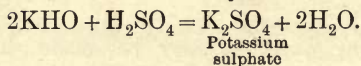
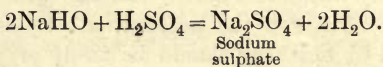
* The compound known as Porrier's Orange No. 3 is the best; 1 gram per litre makes a good solution.

EXAMPLE.—10 c.c. of caustic soda solution required 12·3 c.c. of sulphuric acid solution, and 10 c.c. of caustic potash solution required 8·7 c.c. of sulphuric acid solution.

Since each solution is known to contain 10 grams of the compound in 1,000 c.c., 0·01 gram is contained in 1 c.c.

∴ 0·1 gram of caustic soda neutralizes 0·123 gram of sulphuric acid, and 0·1 gram of caustic potash 0·087 of the acid.

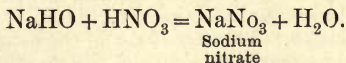
These weights may be compared directly with the equations :



Also $\frac{0\cdot123}{0\cdot087} = 1\cdot41$ = the ratio of the weights of acid required to neutralize the same weight of the alkalies.

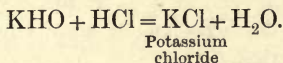
Experiments with nitric acid and with hydrochloric acid may be made in the same way, and the results compared.

EXAMPLE.—10 c.c. of caustic soda solution required 15·6 c.c. of nitric acid solution, and 10 c.c. of caustic potash solution required 11·2 c.c. of nitric acid solution.



Also $\frac{0\cdot156}{0\cdot112} = 1\cdot39$ = ratio of weights of nitric acid required to neutralize the same weight of the alkalies.

EXAMPLE.—10 c.c. of the caustic soda solution required 9·1 c.c. of hydrochloric acid solution, and 10 c.c. of the caustic potash solution required 6·5 c.c. of hydrochloric acid solution.



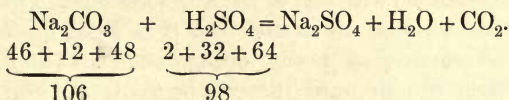
The ratio is $\frac{0\cdot91}{0\cdot65} = 1\cdot41.$

It is evident from the above results that, if equal weights of two bases are used to neutralize different acids, the ratio of the weights of the acids neutralized is constant. This fact was recognised as early as the latter part of the eighteenth century, and work done in this direction by Richter and others helped to lay the foundation of the first law of chemical combination, which is stated on p. 47.

Preparation of Solutions.—In making an acid or an alkaline solution of known strength, it is convenient to add more than the required quantity of the compound, and after determining the actual weight present in a given volume, to bring the whole to the proper strength by the addition of a calculated volume of water. The following proportions may be used, and a large or small volume of the solution prepared as required.

| | | |
|-----------------------------|----------|--------------------------------------|
| Concentrated sulphuric acid | 7 c.c. | } 800 c.c. of water in each case. |
| „ nitric acid | 12 „ | |
| „ hydrochloric acid | 25 „ | |
| Caustic soda | 10 grams | |
| „ potash | 10 „ | |

The strength of an acid solution is usually determined by taking advantage of its reaction with pure sodium carbonate. With sulphuric acid this is :



The carbonate during its decomposition neutralizes the acid, and by using the methyl-orange indicator, the exact amount of acid to be added is readily controlled. From the equation it is clear that 106 parts by weight of Na_2CO_3 neutralize 98 parts by weight of H_2SO_4 ; $\therefore \frac{106}{98} = 1.082 =$ the weight of carbonate required to neutralize 1 part by weight of the acid; and 0.2164 gram is required for 0.2 gram of the acid.

If, then, 0.2164 gram of pure sodium carbonate is dissolved in about 100 c.c. of water, one drop of methyl orange added, and the sulphuric acid solution run in from a burette until the colour change takes place, the volume of the acid solution used will contain exactly 0.2 gram of H_2SO_4 . The whole volume of the remaining solution may then be measured, and the necessary volume of water added to bring it up to the proper strength.

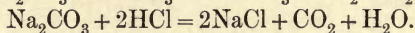
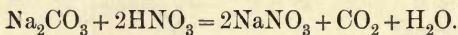
If V = the volume of the remaining acid solution, and v = the volume used to neutralize 0.2164 gram of carbonate,

$$\text{then } \frac{V}{v}(20-v) = \text{volume of water to be added.}$$

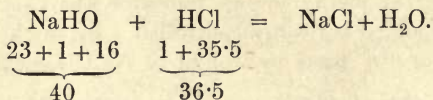
EXAMPLE.—Volume of remaining solution = 750 c.c.; volume used to neutralize = 17 c.c.

$$\therefore \frac{750}{17}(20-17) = \frac{750 \times 3}{17} = 132 \text{ c.c. of water to be added.}$$

The strengths of the other acid solutions can be determined in a similar manner by using the equations:



The atomic weights may be taken from the table in the appendix. The strength of the alkaline solutions are then readily determined with one of the acid solutions. Twenty c.c. of the soda solution are transferred to a flask, diluted with water, and one drop of methyl orange added. The standard acid is then run in until the colour changes. For hydrochloric acid and caustic soda the reaction is expressed by the equation:



$$1 \text{ gram of HCl} = \frac{40}{36.5} = 1.096 \text{ gram of NaHO.}$$

Then the number of cubic centimetres of acid required multiplied by 0.01096 gives the weight of NaHO in 20 c.c. of the solution, and a simple calculation determines the volume of water to be added to the alkaline solution to bring it down to 1 c.c. = 0.01 gram of NaHO. Since each solution contains 10 grams of the pure compounds in 1,000 c.c., the bottles may be labelled as follows :

Sulphuric acid, 1 c.c. = 0.01 gram H_2SO_4 , etc.

NEUTRALIZATION BY INSOLUBLE OXIDES.

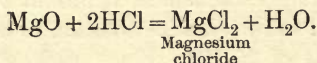
The majority of the oxides insoluble in water are dissolved more or less readily by the common acids, and the corresponding salts are formed. If, however, the salt to be formed is insoluble in the acid solution, dissolution does not take place, and the action between the oxide and the acid is somewhat slow, but, as a rule, the salt is formed on continued digestion with the acid.

Some oxides which will withstand a high temperature without fusing dissolve very slowly after they have been strongly ignited. This is probably due to a closer aggregation of the molecules, by which they become more complex in character and more difficult to decompose. This increase in *molecular* complexity is known as *polymerization*. Strongly ignited ferric and chromic oxides are examples.

Magnesia—EXP. 77.—Put 20 c.c. of dilute hydrochloric acid (1 to 1) into a porcelain basin, and test it with blue litmus-paper. Then add magnesia a little at a time; stir well with a glass rod between each addition, and continue the addition until some of the powder is left undissolved. Test the solution with the litmus-paper, and, if it turns red, boil the solution slowly for a minute or two to see if the residue is dissolved. Filter the liquid to clear it, evaporate it down to half the bulk, and set it aside to crystallize.

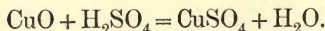
The crystals are usually small and not very distinct. If the solution is evaporated carefully to dryness, and the dry mass exposed to the air, it absorbs moisture, and becomes quite moist. It is a deliquescent salt. The magnesium oxide, MgO ,

dissolves in the acid liquid, and during its dissolution neutralizes the acid. It, therefore, establishes its claim to be a basic oxide.

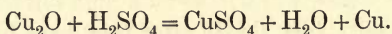


A similar experiment may be made with sulphuric acid and magnesia, and the magnesium sulphate formed is readily crystallized. Its formula is $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Copper Oxide—EXP. 78.—Put 2 grams of black oxide of copper into a large test-tube, and add 15 c.c. of dilute sulphuric acid (1 to 6). Boil the solution gently until the whole of the oxide has dissolved or until the residue becomes distinctly red. Commercial black oxide of copper usually contains a little of the red oxide, which is not completely dissolved by sulphuric acid, and a residue of red metallic copper is left. Filter the solution into a porcelain dish, and, if it is deep blue in colour, set it aside to crystallize; but if only light blue, evaporate it to about half the bulk before setting it aside.



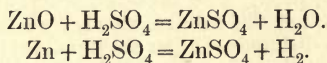
The change with the red oxide is shown thus:



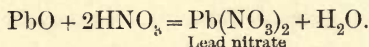
The blue crystals (blue vitriol) have the composition $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Zinc Oxide—EXP. 79.—Repeat the last experiment, using zinc white, ZnO , in place of black oxide of copper. Also, dissolve 2 grams of zinc in dilute sulphuric acid, and set the two solutions aside to crystallize.

On comparison the crystals are found to be exactly the same. Zinc sulphate (white vitriol), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, is formed in each case. Compare the equations:



Oxide of Lead—EXP. 80.—Put 5 grams of lead oxide into a test-tube, add 20 c.c. of dilute nitric acid (1 to 5), and heat the tube gently until the oxide is dissolved. Filter the solution into an evaporating basin, and set it aside to crystallize. Examine the crystals.



The lead nitrate crystals contain no water of crystallization, and the formula of the crystalline salt is $\text{Pb}(\text{NO}_3)_2$. Lead sulphate, PbSO_4 , is insoluble in dilute sulphuric acid, but on boiling the oxide for a few minutes with the moderately strong acid, an appreciable quantity of the sulphate is formed. Hot hydrochloric acid also dissolves lead oxide with formation of the chloride, but the salt largely separates from its solution on cooling.

EXP. 81.—Boil a little lead oxide with moderately strong sulphuric acid (1 to 3) for a few minutes; allow the test-tube to stand until the liquid becomes clear; note the layer of white sulphate upon the yellow residue of unchanged oxide. Repeat the experiment with dilute hydrochloric acid (1 to 1). When the lead oxide is all dissolved set the solution aside to cool, and note the rapid separation of lead chloride crystals.

Water of Crystallization.—Potassium, sodium, and lead nitrates crystallize from their solutions just as they are formed; but zinc, copper, and magnesium sulphates, when they crystallize, carry out with them definite quantities of water. This is called water of crystallization, and is associated with the salts in a very definite manner. It may be taken as a general statement that when a given salt crystallizes under normal conditions it always takes out with it the same proportion of water. The composition of a crystalline salt is constant, but the relation between the salt and its water of crystallization is not so intimate as that between the elements of the salt itself. It is not so intimate even as that between an oxide and the elements of water in its hydroxide. This is shown in the formula by keeping the water separate. Thus: crystallized copper sulphate is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

In general, crystalline salts are freely soluble in water, but there is a limit, differing with different salts, to the quantity of the solid dissolved by a given weight of water. The solubility of a salt, or other solid, is usually stated in terms of parts by weight of cold water required to dissolve 1 part by weight of the solid. Thus potassium nitrate dissolves in

7 parts, zinc sulphate in 2.5 parts, and potassium chlorate in 20 parts of cold water.

In most cases the salt is much more soluble in hot than in cold water, and the cold saturation point is thus easily exceeded. As the solution cools the excess above that which the cold solution will hold tends to separate in the solid state—*i.e.*, to crystallize. But it is possible for the solutions to become quite cold without crystallization setting in. Such a solution is super-saturated, and will crystallize rapidly when once the action is started. A small crystal of the same substance dropped in is usually sufficient to set up the action, and even a speck of dust may form a nucleus for the initial crystals to form round. Generally, if the solution is above the cold saturation point, and cools slowly, the crystallization commences slowly, and the final crystals are larger and better developed. If the solution is too strong the crystallization will be rapid and the crystals very small, forming a powder when dry. When once crystals are formed in the solution they continue to grow, and the dissolved solid is reduced somewhat below the point of cold saturation; but it is impossible to separate the whole of the solid from the solution, for there is a limit at which the solid dissolves from the crystals already formed as fast as it is deposited upon them. The residual solution from which the crystals have separated is called the “mother liquor.”

It will be readily understood that if two solids differ in solubility, it is possible to separate a mixture of them by repeated crystallization, as the more soluble one will not crystallize as rapidly as the less soluble one under the same conditions. Also, a small quantity of one soluble body can be separated from a large quantity of another. These facts are taken advantage of in the purification of salts by repeated crystallization. Some salts dissolve almost as readily in cold as in hot water. That is, their solubility increases very little with a rise in the temperature at which the solution is effected. Common salt is an example. Others, again, seem to

become less soluble after a certain temperature is passed. This is so with sodium sulphate, which, below 33°C ., crystallizes with 10 molecules of water, thus: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. But when a solution which would barely crystallize at ordinary temperatures is raised above 33°C ., small crystals of the anhydrous (waterless) salt, Na_2SO_4 , are deposited. From this it would seem that above 33°C . the ordinary crystallized salt does not exist, and when the point of saturation for Na_2SO_4 is passed crystals are formed.

But this is really a case of equilibrium between the solid and the solvent liquid, and comes within the scope of the phase rule enunciated by Willard Gibbs. For information on this subject the student is referred to recent works on physical chemistry.

Crystals.—A fully-developed crystal is a solid of definite geometrical shape, bounded generally by plane surfaces, which join each other and form solid angles. These surfaces are the faces of the crystals, and an angle formed by the intersection of two or more of these faces is invariable for the same crystalline form. It is possible for a number of different substances to crystallize in the same form, so that a classification of crystals can be made. Thus common salt crystallizes in the form of cubes, in which all the angles are right angles, and therefore equal. Iceland spar crystallizes in rhombs, in which the opposite angles only are equal. Quite a number of other bodies crystallize in the same forms. All the known crystalline forms have been classified into six systems, and the expert crystallographer is able, from the measurement of its angles and the position of its faces, to relegate a particular crystal to its proper system. But the subject is a wide one, and the student must be satisfied at this stage with such information as he can get by an examination of the crystals he produces.

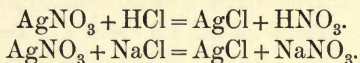
When crystallization takes place *en masse*, as in ordinary experiments, the individual crystals interfere with each other,

and imperfect forms are obtained ; but such parts as are well defined are perfect in themselves, and serve to establish the form. To obtain a perfect crystal of considerable size it is necessary to pick out a small perfect one, and then *nurse* it in a saturated solution of the same salt.

Insoluble Salts.—Some salts are practically insoluble in water, and there is a very easy way of forming them by taking advantage of this property. A solution of a soluble salt of the metal is simply mixed with a solution of the acid, or a solution of a soluble salt of the acid and another metal. The possibility of the formation of the insoluble salt is thus assured, and it immediately commences to separate from the solution as a *precipitate*, which may be crystalline, curdy, or granular.

EXP. 82.—Pour a few cubic centimetres of a solution of silver nitrate into a clean test-tube and add to it dilute hydrochloric acid, a little at a time, with vigorous shaking between each addition, as long as a precipitate separates. Repeat the experiment, using a solution of common salt in place of the hydrochloric acid. Filter, wash and dry the solid salt.

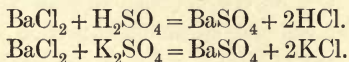
The white curdy solid is silver chloride, and its formation is expressed by the equations :



Silver chloride is not soluble in nitric acid.

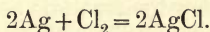
EXP. 83.—Repeat the last experiment, using a solution of barium chloride and dilute sulphuric acid, or a solution of potassium sulphate in place of the acid.

The white, finely-divided solid is barium sulphate, and it is insoluble in hydrochloric or nitric acid :



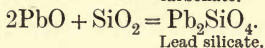
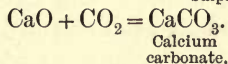
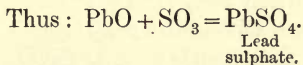
These reactions are used as tests for hydrochloric and sulphuric acids and their soluble salts.

Direct Union of Elements to form Salts.—Salts of hydrochloric acid may be formed by the direct union of the metals with chlorine. This has been already illustrated in the experiments with chlorine. Thus, when chlorine gas is passed over finely-divided silver, the chloride of the metal is formed :



Bromine and iodine act similarly, but not so readily, as chlorine.

Direct Union of Oxides to form Salts.—In the case of some oxyacids it is possible to form their salts by the direct union of the acid-forming and the basic oxides.



These reactions indicate that there cannot be any strong objection to writing the formulæ of the compounds in such a way as to show the combination of the two oxides. For example : $\text{PbO}.\text{SO}_3$; $\text{CaO}.\text{CO}_2$; $2\text{PbO}.\text{SiO}_2$. Sometimes it is convenient to use such formulæ, especially in the case of silicates. See Chap. XIV.

The decomposition of a carbonate by an acid, in which the salt of the acid and of the metal in the carbonate is formed, furnishes another general method of forming salts. Illustrations of this method will be found in Chap. X. The following is a summary of the chief modes of salt formation : (1) Direct union of elements ; (2) direct union of acid-forming and basic oxides ; (3) replacement of hydrogen in an acid by a metal ; (4) reaction between acids and bases ; (5) formation of insoluble salts by precipitation ; (6) decomposition of carbonates by acids.

Nomenclature of Salts.—In the systematic naming of

salts, terminations are used, as in the case of oxides. The assumption that acids are also salts of the displaceable hydrogen they contain, and are, therefore, of the same general character as the compounds formed by the replacement of such hydrogen by metals, is very useful.

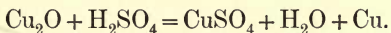
According to this view hydrochloric acid, HCl , is also hydrogen **chloride**, and common salt, sodium **chloride**. Similarly we have **bromides**, **iodides**, etc. Thus, when the acid and its salts contain two elements only, the termination **-ide** is used to designate the group to which the salt belongs, and the name of the metal to particularize the salt. Potassium bromide, KBr ; zinc iodide, ZnI_2 ; bismuth chloride, BiCl_3 , are examples. Nitric acid, HNO_3 , is also hydrogen **nitrate**, and saltpetre is potassium **nitrate**.

But there is also another acid, HNO_2 , nitrous acid or hydrogen **nitrite**, and its salts are **nitrites**—*e.g.*, potassium nitrite, KNO_2 .

Thus when there are two acids containing the same elements, but in different proportion, the terminations **-ous** and **-ite** are used for the lower acid and its salts, and **-ic** and **-ate** for the higher compounds. Similarly sulphurous acid gives **sulphites**, and sulphuric acid, **sulphates**. When there is only one oxy-acid of a given element the higher terminations are used; *e.g.*, carbonic acid gives carbonates. The student is advised to keep the idea of acids as salts of hydrogen well in mind, as it will assist him in getting a firm grip of the composition and formulæ of salts.

Constitution of Acids.—The molecule of an acid may be looked upon as consisting of two parts, which are represented graphically thus: $(\text{H})(\text{Cl})$, $(\text{H})(\text{NO}_3)$, $(\text{H}_2)(\text{SO}_4)$. Now, the second part of the acid molecule is present in the molecule of any salt of the acid, and is characteristic of it; so that the (Cl) , (NO_3) , and (SO_4) groups are characteristic of chlorides, nitrates, and sulphates generally. The same may be said of other acids and their salts.

There is good reason to believe that when an acid or its salt is dissolved in a very large quantity of water, its molecules split up or *dissociate* into the parts mentioned above. These parts are called ions; and even when the solution is moderately strong, an average number of molecules are believed to be constantly in this state of dissociation, or ionic condition. This matter is closely studied in electro-chemistry, and is mentioned here in order to justify the statements made in the last paragraph. It has already been stated that some metals form two basic oxides, and when these dissolve in a given acid two distinct salts are formed. Thus there are two sulphates of iron: **ferrous** sulphate, FeSO_4 , and **ferric** sulphate, $\text{Fe}_2(\text{SO}_4)_3$; also two chlorides of mercury, **mercurous** chloride, Hg_2Cl_2 , and **mercuric** chloride, HgCl_2 . But it must not be inferred that when there are two basic oxides of a metal there are also two salts of any acid. For example, the two oxides, Cu_2O and CuO , both give copper sulphate, CuSO_4 , when heated with dilute sulphuric acid, but the first is decomposed and leaves a deposit of copper. Thus:



There are, however, two chlorides of copper, Cu_2Cl_2 and CuCl_2 .

Some old-fashioned distinctive names which are still used may be mentioned here. Thus ferrous sulphate is also the **protosulphate** of iron, and ferric sulphate the **persulphate** of iron. Also **subchloride** of mercury is the same as mercurous chloride, and the perchloride is the mercuric salt.

Basicity of Acids.—The valency of metals has already been defined as their atom-replacing power, and is measured by the number of atoms of hydrogen replaced by one atom of the metal. Now, if acids are salts of hydrogen, it is easy to see from their formulæ that the number of atoms of the replaceable hydrogen differs in different acids, and that the

property known as the basicity of the acid depends on this number.

| | | | | |
|------------------|--------------------------|----------------|--------|--------------|
| Nitric acid, | HNO_3 | is mono | basic. | |
| Sulphuric acid, | H_2SO_4 | is di | „ | } Polybasic. |
| Phosphoric acid, | H_3PO_4 | is tri | „ | |
| Silicic acid, | H_4SiO_4 | is tetr | „ | |

With a monobasic acid the hydrogen is all replaced in one reaction, and the **normal** salt only is formed. But with a **poly**basic acid the hydrogen may be replaced in two or more distinct reactions, thus giving rise to two or more distinct salts. Those in which hydrogen is present are called **acid** salts.

Potassium hydrogen sulphate, KHSO_4 , acid salt.

Potassium sulphate K_2SO_4 , normal salt.

Sodium dihydrogen phosphate, NaH_2PO_4 , acid salt.

Disodium hydrogen phosphate, Na_2HPO_4 , acid salt.

Trisodium phosphate, Na_3PO_4 , normal salt.

The second salt of phosphoric acid above mentioned is the common sodium phosphate. Sometimes salts are formed in which an excess of the acid-forming oxide is present. Such compounds are *anhydro-acid* salts. The well-known example is potassium bichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, which may also be written $\text{K}_2\text{CrO}_4\text{CrO}_3$. Potassium chromate, K_2CrO_4 , is the normal salt.

Similarly some salts contain an abnormal quantity of the basic oxide or hydroxide, and are then called *basic* salts. The green mineral malachite is a basic carbonate of copper, $\text{CuCO}_3\cdot\text{CuH}_2\text{O}_2$.

Only one acid of carbon has been mentioned, but a large number of acids are found in organized matter, both animal and vegetable, or are formed during organic changes. These invariably contain carbon and hydrogen, but the whole of the hydrogen is not as a rule replaceable in the same manner as that of a mineral acid. This is well illustrated in the case of *acetic* acid and its salts. The empirical formula of this

acid is $\text{H}_4\text{C}_2\text{O}_2$, but to show its basicity it must be written $\text{H.C}_2\text{H}_3\text{O}_2$, for it contains only one atom of replaceable hydrogen which is written first. Thus the formula for lead acetate (sugar of lead) is $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. On the other hand, oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is dibasic. The salts of these acids are termed respectively acetates and oxalates.

Double Salts.—It is found that when some soluble salts are dissolved together in approximately molecular proportions they also crystallize together in strictly molecular proportions when the solution is sufficiently concentrated. In fact, so constant is the composition of these double compounds, that they are regarded as definite salts. The alums are the most common and the best illustrations of these very interesting bodies. Common alum is a double sulphate of potassium and aluminium, and its empirical formula is $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The two sulphates are potassium sulphate, K_2SO_4 , and aluminic sulphate, $\text{Al}_2(\text{SO}_4)_3$. So that the formula which shows the composition best is obtained by doubling the above thus, $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$. Potassium sulphate is easily crystallized alone, but the aluminium sulphate only with difficulty, and the forms of the crystals are quite distinct. On dissolving the salts together in molecular proportions, and allowing the solution to crystallize, the double salt is obtained in crystals of the regular octahedron form.

EXP. 84.—Put 1 gram of alumina, Al_2O_3 , into a small beaker, add 10 c.c. of dilute sulphuric acid (1 to 3), and boil slowly until the solid disappears, and a somewhat milky-looking solution is obtained. Dissolve 1 gram of caustic potash in 10 c.c. of water, add this solution to the first, raise the whole to boiling, and filter the solution into a porcelain basin. Set it aside to crystallize. Examine the crystals under a lens, and note their characteristic shape. Set aside the best for reference.

The crystals are usually well defined, if the solution is not too concentrated, and the crystallization takes place slowly. If caustic soda is used in the above experiment in place of potash, exactly similar crystals are obtained. The two salts

cannot be distinguished from each other by their crystalline form. Also, if ferric oxide, Fe_2O_3 , is substituted for alumina, light green crystals are obtained, which cannot be distinguished from the others by their crystalline form.

EXP. 85.—Dissolve 5 grams of potassium bichromate in 25 c.c. of water, and add 1 c.c. of strong sulphuric acid. Prepare sulphur dioxide, and pass the washed gas (p. 95) through the solution until it turns deep green in colour. Pour it into a large porcelain dish, and set it aside to crystallize. Compare the crystals of chrome alum with those of common alum from Exp. 84.

It will be noticed that the two metals in the sulphates are monad and triad respectively; any similar metal may be substituted in the compound without altering its form. Thus silver and the monad group ammonium (NH_4) may take the place of potassium, and the triad metals, chromium and manganese, that of aluminium. The general formula is $\text{M}'\text{M}'''(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ where M' and M''' are monad and triad atoms respectively.

If a crystal of common alum is put into a solution of iron alum it increases in bulk; the enlarged crystal may then be transferred in turn to solutions of chrome alum and manganese alum, in each of which there is a further growth, but the final crystal keeps its fundamental form. Further, if a mixture of various alums is crystallized, one crop of crystals containing the different compounds is obtained.

Another class of double salts of practical importance contain ammonium or potassium sulphate with iron, nickel, or zinc sulphate. The well-known examples are ferrous ammonium sulphate $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and nickel ammonium sulphate, $(\text{NH}_4)_2\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

Isomorphism.—The similarity of form of different crystallized compounds is looked upon as an indication of similarity in the constitution of their molecules, and such compounds are said to be **isomorphous**, which means, literally, of “equal form.” It is not confined to the double salts described above, for two single salts crystallized separately may have the same

crystalline form. They are then judged to be made up of similarly constituted molecules.

This supposed similarity of the molecules of isomorphous compounds suggests similarity between the atoms of those elements which are able to replace each other in them without altering the crystalline form of the compounds; and they are also considered to be isomorphous. Thus, Na, K, Ag; and Al^{'''}, Fe^{'''}, Cr^{'''} replace each other in the alums. They are regarded as two groups of isomorphous metals. Similarly, Zn^{''}, Fe^{''}, Ni^{''} are isomorphous with regard to the class of isomorphous salts of which $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is a well-known example. This principle of isomorphism has been of considerable value in helping to fix the atomic weights of a number of the metals. It has also been used to explain some of the changes which take place during the cooling and solidification of a molten mass of mixed metals. A mixture of isomorphous salts cannot be separated from each other by crystallization, as they are deposited from the solution together; but mixtures of non-isomorphous compounds may be so separated if their solubility in the mother liquor differs. Similar remarks apply to isomorphous and non-isomorphous metals in a molten alloy.

Action of Heat upon Salts.—Water of crystallization is driven off, usually at temperatures very little above the boiling-point, 100° C. But sometimes one or more molecules of water hold more tenaciously to the salts, and require a higher temperature for their separation. Further heating of the anhydrous salt may cause it to melt and even to volatilize; or it may be decomposed into simpler compounds, and, in a few cases, into its elements.

EXP. 86.—Weigh exactly 2 grams of powdered crystallized copper sulphate in a dry porcelain crucible, or on a clay roasting dish, and heat it on a pipeclay triangle over a Bunsen flame until it turns white. Allow the crucible to cool and reweigh it. Put the crucible into a gas muffle, and keep it at a fair red heat for twenty minutes,

or until the residue is quite black. Allow the crucible to cool and reweigh it. The residue is black oxide of copper.

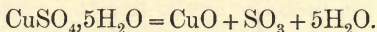
EXAMPLE.—

| | | | |
|---------------------------|----------|---|---------|
| Weight of crucible + salt | = 13.140 |) | = 0.718 |
| „ after first heating | = 12.422 | | |
| „ „ second „ | = 11.776 | | = 0.646 |
| „ of crucible | = 11.140 | | = 0.636 |

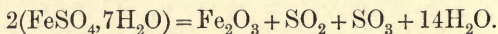
First loss = 0.718 gram H_2O ; second loss = 0.646 gram SO_3 ; residue = 0.636 gram CuO , and these are the weights of the three oxides in 2 grams of the compound. Now, divide each weight by the molecular weight of the oxide to which it belongs. $\text{CuO} = 79$; $\text{SO}_3 = 80$; $\text{H}_2\text{O} = 18$.

$$\text{Then, } \frac{0.718}{18} = 0.0399; \quad \frac{0.646}{80} = 0.008; \quad \frac{0.636}{79} = 0.008.$$

These ratios show the relation between the molecules of the oxides in the crystallized salt, and are readily reduced to whole numbers by dividing each by the lowest. This gives 1 CuO : 1 SO_3 : 5 H_2O , and the formula may be written, $\text{CuO} \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$. The complete reaction is expressed by the equation:



Four molecules of water are separated at a temperature about 100°C .; but the last molecule clings until the temperature exceeds 200°C . A similar experiment may be made with crystallized ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which gives the following reaction when heated:



Most of the sulphates of the common heavy metals are decomposed in a similar manner, but a number of others, including those of potassium, barium, lead, etc., may be heated very strongly without undergoing decomposition.

The **Nitrates** are all more or less readily decomposed when heated. Oxides of nitrogen and oxygen are set free, and a residue of the oxide of the metal left. Nitrates of silver and mercury are reduced to the metallic state.

The **Chlorides** fuse more or less readily, and volatilize when strongly heated. Some are decomposed with liberation of chlorine, and are thus reduced, either to a lower chloride or to the metallic state.

The **Carbonates** of sodium and potassium will withstand a high temperature without decomposition. The other common carbonates are split up into metallic oxides and carbon dioxide. Barium carbonate requires a bright red heat for its decomposition.

A number of well-known acids are represented by only a few common salts, but as these are of considerable importance a list of them is given below.

| ACID. | FORMULA. | SALT. | FORMULA. | COMMON NAME. |
|----------------|-----------------------------------|-----------------------------|--|----------------------|
| Sulphurous | H_2SO_3 | Sodium sulphite | $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$ | Sulphite of soda |
| Thio-sulphuric | $\text{H}_2\text{S}_2\text{O}_3$ | Sodium thio-sulphate | $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ | Hyposulphite of soda |
| Phosphoric | H_3PO_4 | Disodium hydrogen phosphate | $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ | Phosphate of soda |
| Chloric | HClO_3 | Potassium chlorate | KClO_3 | Chlorate of potash |
| Chromic | H_2CrO_4 | Potassium chromate | K_2CrO_4 | Chromate of potash |
| | | Potassium bichromate | $\text{K}_2\text{Cr}_2\text{O}_7$ | |
| Permanganic | $\text{H}_2\text{Mn}_2\text{O}_8$ | Potassium permanganate | $\text{K}_2\text{Mn}_2\text{O}_8$ | |
| Metaboric | HBO_2 | Acid sodium borate | $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ | Borax |
| Nitrous | HNO_2 | Potassium nitrite | KNO_2 | Nitrite of potash |
| Hydrobromic | HBr | Potassium bromide | KBr | |
| Hydriodic | HI | Potassium iodide | KI | |
| Hydrofluoric | HF | Calcium fluoride | CaF_2 | Fluor spar |

Salts of these acids and the common metals are easily obtained by one or other of the usual methods of salt formation.

SUMMARY.

The basic oxides of the metals are a very important class of compounds. They react with acids to form salts. In the

TABLE OF COMMON OXIDES AND SALTS.

| | | ACIDS. | | | |
|---------------|---|--|---|--|--|
| METALS. | OXIDES. | HYDROCHLORIC ACID, HCl. | NITRIC ACID, HNO ₃ . | SULPHURIC ACID, H ₂ SO ₄ . | CARBONIC ACID, H ₂ CO ₃ . |
| | | CHLORIDES. | NITRATES. | SULPHATES. | CARBONATES. |
| Aluminium ... | Al ₂ O ₃ | Al ₂ Cl ₃ or AlCl ₃ | Ba(NO ₃) ₂ | Al ₂ (SO ₄) ₃ ·8H ₂ O | |
| Antimony ... | Sb ₂ O ₃ , Sb ₂ O ₄ , Sb ₂ O ₅ | SbCl ₃ , SbCl ₅ | Bi(NO ₃) ₃ ·5H ₂ O | BaSO ₄ | BaCO ₃ Bi ₂ O ₃ ·CO ₂ , basic CdCO ₃ CaCO ₃ |
| Barium ... | BaO, BaO ₂ | BaCl ₂ ·2H ₂ O | Cd(NO ₃) ₂ | CdSO ₄ | |
| Bismuth ... | Bi ₂ O ₃ | BiCl ₃ | Ca(NO ₃) ₂ ·H ₂ O | CaSO ₄ ·2H ₂ O | |
| Cadmium ... | CdO | CdCl ₂ ·2H ₂ O | Cr ₂ (NO ₃) ₆ | Cr ₂ (SO ₄) ₃ ·5H ₂ O | |
| Calcium ... | CaO | CaCl ₂ ·6H ₂ O | Co(NO ₃) ₂ ·6H ₂ O | CoSO ₄ ·7H ₂ O | |
| Chromium ... | CrO, Cr ₂ O ₃ | Cr ₂ Cl ₆ | Cu(NO ₃) ₂ ·6H ₂ O | CuSO ₄ ·5H ₂ O | |
| Cobalt ... | CoO, Co ₂ O ₃ | CoCl ₂ ·6H ₂ O | | | 2CuO·CO ₂ ·H ₂ O, basic |
| Copper ... | Cu ₂ O, CuO | Cu ₂ Cl ₂ | Fe(NO ₃) ₃ ·6H ₂ O | FeSO ₄ ·7H ₂ O | FeCO ₃ |
| Gold ... | FeO, Fe ₂ O ₄ , | AuCl, AuCl ₃ | Fe ₂ (NO ₃) ₆ ·12H ₂ O | Fe ₂ (SO ₄) ₃ | |
| Iron ... | Fe ₂ O ₃ | FeCl ₂ , Fe ₂ Cl ₆ | Pb(NO ₃) ₂ | PbSO ₄ | 3PbO·2CO ₂ ·H ₂ O basic |
| Lead ... | PbO, Pb ₃ O ₄ , PbO ₂ | PbCl ₂ | Mg(NO ₃) ₂ ·6H ₂ O | MgSO ₄ ·7H ₂ O | MgCO ₃ |
| Magnesium ... | MgO | MgCl ₂ ·6H ₂ O | Mn(NO ₃) ₂ | MnSO ₄ ·5H ₂ O | MnCO ₃ |
| Manganese ... | MnO, Mn ₃ O ₄ , MnO ₂ | MnCl ₄ | Hg(NO ₃) ₂ ·H ₂ O | HgSO ₄ , Hg ₂ SO ₄ | |
| Mercury ... | HgO | HgCl ₂ , Hg ₂ Cl ₂ | Hg ₂ (NO ₃) ₂ ·2H ₂ O | | |
| Nickel ... | NiO | NiCl ₂ ·9H ₂ O | Ni(NO ₃) ₂ ·6H ₂ O | NiSO ₄ ·7H ₂ O | |

| | | | | | |
|---------------|-------------------|---------------------------------------|-----------------------------------|--|--|
| Potassium ... | K ₂ O | KCl | KNO ₃ | K ₂ SO ₄ , KHSO ₄ | K ₂ CO ₃ , KHCO ₃ |
| Platinum ... | Ag ₂ O | PtCl ₄ | AgNO ₃ | Ag ₂ SO ₄ | N ₂ CO ₃ , 10H ₂ O, |
| Silver ... | Na ₂ O | AgCl | NaNO ₃ | NaHSO ₄ | NaHCO ₃ |
| Sodium ... | | NaCl | | SrSO ₄ | SrCO ₃ |
| Strontium ... | SrO | SrCl ₂ , 3H ₂ O | Sr(NO ₃) ₂ | Sn(SO ₄) ₂ | 5ZnO · 2CO ₂ · 3H ₂ O |
| Tin ... | SnO ₂ | SnCl ₂ , SnCl ₄ | Zn(NO ₃) ₂ | ZnSO ₄ , 7H ₂ O | basic |
| Zinc ... | ZnO | ZnCl ₂ | | (NH ₄) ₂ SO ₄ , | (NH ₄) ₂ CO ₃ , |
| Ammonium ... | | NH ₄ Cl | NH ₄ NO ₃ | NH ₄ HSO ₄ | (NH ₄)HCO ₃ |

NOTES ON THE TABLE.

1. Solubility in water and acids.

Oxides.—Na₂O and K₂O are readily soluble; BaO, SrO, CaO are somewhat soluble; and PbO is slightly soluble in water. All are soluble in one or other of the common acids.

Chlorides.—AgCl, Cu₂Cl₂ are insoluble in water, but soluble in hot HCl; PbCl₂ is soluble in hot water. Bi and Sb form insoluble oxychlorides with excess of water. All others are soluble.

Nitrates.—Bi(NO₃)₃ forms an insoluble basic salt with excess of water. All others are soluble.

Sulphates.—BaSO₄ is insoluble in water and acids. PbSO₄, SrSO₄, and CaSO₄ are slightly soluble in water, but more soluble in acids. All others are soluble in water.

Carbonates.—The salts of K and Na are soluble, but all the others are insoluble in water free from CO₂. All are soluble in acids with evolution of CO₂ and formation of the salts of the acids used.

11 2. The water of crystallization is shown in the formulæ when it is present in the common forms of the salts.

3. Ammonium salts are all soluble in water, and undergo decomposition when heated, except the chloride, and this volatilizes apparently unchanged.

majority of cases the basic character of the oxide disappears along with the acid character of the acid, and neutral bodies are formed. Metallic hydroxides contain the elements of water in addition to the oxides. They act in the same way towards acids as the corresponding oxides. The peroxides undergo partial decomposition when heated, and oxygen is liberated. The acid-forming oxides unite with water to form acids, and in this respect they resemble the acid-forming oxides of non-metals. Salts are formed in a variety of ways, but a given salt always has the same composition, however it may be formed. The quantitative relations of neutralization are just as definite as those of any other mode of chemical action.

QUESTIONS.

1. How are oxides usually classified? Give examples.
2. What are the general effects of adding basic oxides to acid solutions?
3. Explain how an acid salt and a normal salt differ from each other.
4. How are crystals usually formed? Why are some salts said to be isomorphous?
5. What is meant by the nomenclature of compounds? Give examples to illustrate your answer.
6. Describe three ways of forming zinc sulphate.
7. Is there any similarity between the basicity of an acid and the valency of a metal?
8. Give a short account of the principle of isomorphism.

CHAPTER X

CARBON AND ITS COMPOUNDS

THE element carbon is a very common and useful substance. It is a constituent of all animal and vegetable bodies ; and is present among the rocks and minerals of the earth's crust in all natural carbonates, of which the calcium salt CaCO_3 is by far the most abundant. It is also the principal constituent of coal, which is the product of the very slow decay of vegetable matter out of contact with air. Such matter contains carbon, hydrogen, oxygen, and nitrogen as essential constituents, together with a small quantity of inorganic or earthy matter. Air-dried wood contains about 50 per cent. of carbon and 1.5 per cent. of inorganic compounds ; the remainder is made up of oxygen, hydrogen, and nitrogen. During the extremely slow changes which the original wood has undergone in its conversion to coal, the oxygen and hydrogen, together with some of the carbon, have been largely eliminated. Therefore the residue of coal contains a much higher percentage of carbon than the vegetation from which it was formed. In fact, the oldest variety of coal may be described as impure carbon, containing as it does upwards of 90 per cent. of carbon.

Graphite or *plumbago* is also an impure form of carbon found in the earth's crust ; and the *diamond* is the purest form of natural carbon.

The various oils and fats of animal, vegetable, and mineral origin are extremely rich in carbon.

Charcoal.—When wood is heated in a vessel from which the air is excluded, such as a porcelain crucible with the lid on, a residue very rich in carbon is obtained; it is called charcoal, and is a very useful fuel.

EXP. 87.—Heat a piece of sound wood, about $\frac{1}{2}$ -inch cube, in a porcelain crucible with the lid on until gaseous matter ceases to escape. The crucible should be put on a pipeclay triangle over a Bunsen flame for a few minutes, and the heating finished over the foot blow-pipe. When the crucible is nearly cold, remove the lid and examine the residue.

Grind the piece of charcoal to a fine powder in a clean mortar, put it into a small platinum crucible with a closely-fitting lid, and heat it as strongly as possible for ten minutes in the blow-pipe flame.

The experiment may be made quantitative by weighing the wood before, and the charcoal after, heating.

The charcoal thus obtained contains about 92 per cent. of carbon, 1.5 per cent. of earthy matter, which forms the ash when the charcoal is completely burnt, and some oxygen and hydrogen.

Some carbonaceous bodies are practically free from earthy matter, and furnish very pure charcoal when properly treated. Sugar is a very good illustration of these bodies.

EXP. 88.—Melt some good lump-sugar in a large porcelain crucible; continue the heating until the combustible gas is all expelled, and a black residue of "burnt" sugar is obtained. The total quantity of sugar should be added to the crucible a little at a time as it works down, or it will boil over and make the experiment unsatisfactory.

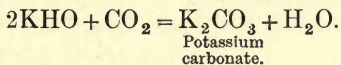
Grind the black residue to a fine powder, and heat it very strongly for ten minutes in a closed platinum crucible, as described above. When cold, transfer the powder to a small stoppered bottle.

The carbon so obtained is not quite pure, but contains about 0.1 per cent. of earthy matter and some oxygen and hydrogen. The gaseous elements can be got rid of by strongly heating the powder in a glass tube through which a stream of dry chlorine gas is made to pass. The heating in contact with chlorine is continued as long as fumes of hydrochloric acid escape from the open end of the tube. A sample of carbon

prepared as described in Exp. 88, and also subjected to the action of chlorine, was found to contain 99·7 per cent. of carbon and 0·1 per cent. of ash.

COMBUSTION OF CHARCOAL.

When charcoal is heated in a good current of air or in oxygen, it burns, and the whole of the carbon in it is converted into carbon dioxide, CO_2 . This compound is a colourless, transparent gas, which dissolves in water, and forms a weak acid solution. It is therefore an acid-forming oxide, and combines with a number of basic oxides to form the salts known as **carbonates**. It is rapidly absorbed by a solution of caustic soda or potash, and forms a carbonate with the alkali which remains in the solution. The reaction is shown by the equation :



This change is taken advantage of in estimating how much carbon dioxide is formed by the combustion of a known weight of carbon. The experiment requires considerable care, and accurate weighings must be made ; but the following description will be readily followed.

EXP. 89.—A small quantity (about 0·1 gram) of the purest charcoal at hand is weighed on a bent strip of platinum foil, which is then pushed into the middle of a glass combustion-tube, A (Fig. 30). One end of A is then connected with the weighed potash bulbs, B, which contain a strong solution of caustic potash, KHO, in water (1 to 2). The other end of A is connected with the drying-tube C, containing small lumps of caustic soda in the limb *a*, and calcium chloride in the limb *b*. The part of the tube directly under the platinum foil containing the charcoal is then heated in a Bunsen flame, and a moderate stream of dry oxygen passed through the apparatus. This is readily effected by using the apparatus shown in Fig. 32. The bottle C is filled with oxygen, and the wash-bottle D, containing a little strong sulphuric acid, is connected with the inlet of the drying-tube C (Fig. 30). The charcoal burns in the oxygen ; the carbon dioxide formed is carried forward by the excess of gas, and is completely absorbed by the potash in B. The difference in

the weight of the platinum foil containing the charcoal, before and after the combustion, gives the weight of carbon burnt, and the difference in the weight of the potash bulbs gives the weight of carbon dioxide absorbed. A small quantity of ash is left on the foil.

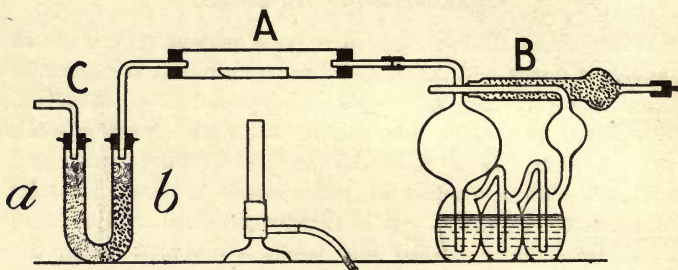


FIG. 30.

For very accurate work a drying-tube must be placed between A and B. Powdered graphite and diamond dust burn very slowly in a glass tube; but a porcelain tube heated in a table furnace (Fig. 8) gives very satisfactory results. When pure carbon is used the ratio, carbon to carbon dioxide, is found to be 12 : 44. That is, 12 parts of carbon combine with 32 parts of oxygen to form 44 parts of carbon dioxide. Therefore its formula is CO_2 .

Experiments made with sugar carbon, purified graphite, and diamond dust give practically the same result, and either of them can be used to determine the composition of carbon dioxide.

Experimental proof is thus furnished of the statement that charcoal, graphite, and diamond are one and the same **chemical** element—*i.e.*, carbon. But there is a very marked difference in their **physical** properties. These variations in the properties of the same element are called **allotropic modifications** (p. 57). The principal variations are in the colour, hardness, and structure of the bodies. The diamond is crystalline and very hard; graphite is crystalline and soft;

charcoal is amorphous—*i.e.*, without crystalline form. Another important difference is that, although the equal weights of the three give the same weight of carbon dioxide, they do not give out the same quantity of heat when burnt. The calorific power of the diamond is less than that of graphite, and of graphite less than that of charcoal. This is probably due to the constitution and aggregation of their molecules. The different forms of carbon can be changed from one to the other. Thus, when a diamond is raised to the temperature of the electric arc, it is converted into a black mass of coke-like carbon. Amorphous carbon, after absorption by heated iron, may be caused to separate from the molten mass in the form of graphite. This form of artificial graphite is known as *kish*. Scales of crystalline graphite are easily recognised on the fractured surface of a piece of grey pig-iron. The carbon goes into the furnace in the form of coke. Amorphous carbon has also been converted into diamond crystals; but those produced up to the present are too small to be of practical use.

CARBONATES.

Native Carbonates.—Limestone, marble, and chalk, which occur in enormous quantities in the earth's crust, are varieties of calcium carbonate, CaCO_3 . The first two are distinctly crystalline in character. Calcite, or Iceland spar, a purer form of the same compound, is found in the form of rhombic crystals, which are sometimes as clear and transparent as glass. Aragonite is another crystalline form of calcium carbonate.

Magnesium carbonate, MgCO_3 , is isomorphous with the calcium salt, and occurs along with it in dolomite, which is usually described as a double carbonate of lime and magnesia. Different specimens of dolomite contain the two carbonates in varying proportions, which is consistent with the formation of isomorphous mixtures (Chap. IX.).

Ferrous carbonate, FeCO_3 , which is the principal constituent

in spathic iron ore and clay ironstone, and manganous carbonate, MnCO_3 , are isomorphous with the calcium and magnesium salts which often accompany them in their ores.

Zinc carbonate, ZnCO_3 , in calamine, and lead carbonate, PbCO_3 , in cerussite, are also important natural carbonates.

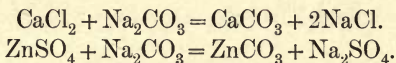
Prepared Carbonates.—Sodium carbonate, Na_2CO_3 , is the most important of these compounds. It is prepared both in the anhydrous form, Na_2CO_3 , and with water in soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Both forms are readily soluble in water. Soda crystals lose water when exposed to the air, and gradually break down to a white powder; they are **efflorescent**. When heated the crystals melt in their water of crystallization, which is then removed by evaporation, and the anhydrous salt is left as a white residue. This melts to a clear liquid at a moderately high temperature. If mixed with the corresponding potassium salt a more readily fusible mass is obtained. Common fusion mixture contains $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$.

The majority of metallic carbonates are either insoluble or only slightly soluble in water, and are precipitated as amorphous solids when a solution of sodium or potassium carbonate is added to solutions of the soluble compounds of the metals. Very often, however, the oxide of the metal separates at the same time, and basic carbonates are formed.

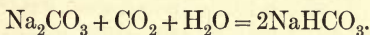
EXP. 90.—Make a solution of sodium carbonate (1 in 10). Pour about 10 c.c. of a solution of calcium chloride, CaCl_2 , into a large test-tube, and add the sodium carbonate solution a little at a time, with shaking, as long as a precipitate forms. Raise the contents of the tube to boiling, filter, and well wash the precipitate on the filter. Dry the filter, and scrape off the white solid calcium carbonate. Repeat the experiment with a solution of zinc sulphate in place of the calcium chloride. Put some of the calcium carbonate in a test-tube, add a little dilute hydrochloric acid, and pour the escaping gas into a test-tube containing a little lime-water. Shake the lime-water to bring it in contact with the gas, and note the milkiness caused by the absorption of carbon dioxide.

Put a little of the dry zinc carbonate into a small test-tube, heat it in the Bunsen flame, and prove that carbon dioxide is evolved.

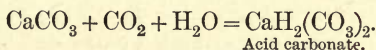
The reactions for the formation of the carbonates are as follows :



Bicarbonates.—These are acid salts, of which the best example is bicarbonate of soda, NaHCO_3 . The normal soluble carbonates have a decidedly alkaline reaction, for the weak, acid-forming oxide, CO_2 , does not neutralize the strong soda base, Na_2O . The acid carbonates are milder because of the excess of CO_2 present. They are readily decomposed at a moderate heat into the normal salts, carbon dioxide, and water. Normal carbonates are converted into the corresponding acid salts when exposed to the action of carbon dioxide and water, and sometimes an insoluble carbonate is thus converted into a soluble one. When carbon dioxide is passed for some time into a solution of sodium carbonate the bicarbonate crystallizes out :



And when the gas is passed through water in which finely-divided calcium carbonate is suspended, the solid passes into solution. The acid carbonate is soluble :

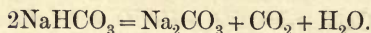


But on boiling the solution the CO_2 is expelled and the normal carbonate precipitated.

ACTION OF HEAT ON CARBONATES.

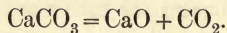
The sodium and potassium compounds are not decomposed at a bright-red heat. Carbonates of Ba, Sr, Ca, and Mg are decomposed at a good red heat into the basic oxides of the metals and carbon dioxide; the barium carbonate requires the highest temperature. Carbonates of the other common metals are decomposed at a still lower temperature. Bicarbonates give off water in addition to carbon dioxide, but in

the case of the alkaline bicarbonates only part of the CO_2 is liberated :



EXP. 91.—Weigh 1 gram of ground marble in a weighed porcelain crucible; heat the crucible, without the lid, in a gas muffle to a bright-red heat for fifteen minutes. When the crucible is cold reweigh it. The loss in weight gives the carbon dioxide driven off. If a muffle cannot be used, heat the crucible over a good circular burner, and finish with five minutes over the foot blow-pipe. In this case a platinum crucible is best.

EXAMPLE.—One gram of marble lost 0.434 gram on being heated for twenty minutes in a gas muffle. Compare this with the equation :



Sodium bicarbonate is readily decomposed in a porcelain crucible heated over a Bunsen burner, and as the commercial salt is comparatively pure, a good result is obtained. Zinc and lead carbonates also furnish good examples. The residue of zinc oxide is quite infusible; but lead oxide is somewhat fusible, and, unless the temperature is carefully regulated, it will soften, stick to the crucible, and spoil it.

When a basic carbonate containing an excess of the anhydrous oxide is heated CO_2 only is driven off, but when the hydroxide forms the excess of the base H_2O is also evolved. In this case the loss includes both carbon dioxide and water. In order to determine the proportions of the three oxides in the salt it is necessary to determine the carbon dioxide by a separate experiment, and then deduct its weight from the total loss on heating.

EXP. 92.—Weigh 1 gram of blue copper carbonate in a weighed porcelain crucible, and heat it over the Bunsen flame until it turns completely black. Allow the crucible to cool, and reweigh it. The loss gives the weight of carbon dioxide and water driven off.

EXAMPLE.—One gram of the blue carbonate lost 0.296 gram when heated for ten minutes over the Bunsen flame.

CARBONATES AND ACIDS.

All carbonates are decomposed by dilute acids with evolution of carbon dioxide, and formation of the salts of the metals in the carbonates and of the acids. If the salt formed is insoluble, or only slightly soluble, in the acid solution, the action soon ceases as the carbonate becomes coated with this insoluble body, which protects it from the acid. Nitric acid is the best general solvent.

Determination of the Weight of CO_2 in a Carbonate.—The apparatus shown in Fig. 27 gives excellent results, and is easy of manipulation. It may be used for any carbonate.

EXP. 93.—Add 10 c.c. of dilute nitric acid (1 to 3) to the flask A (Fig. 27), and fit the parts of the apparatus together. Put the whole on the scale-pan of the balance, and along with it a piece of filter-paper which will conveniently hold 1 gram of the salt. Weigh the whole accurately, then put a gram weight on the weight-pan, and weigh 1 gram of blue copper carbonate on the filter-paper. Fold up the paper containing the salt into a packet which can be readily pushed through the neck of the flask. Take the bung out; remove the stopper from the outlet of the drying-tube; push the packet into the neck of the flask, and then into the body with the tube passing through the bung, rapidly inserting the latter as the packet falls in the acid. When the action is finished, connect the outlet of the drying-tube with the aspirator (Fig. 28), and draw about a litre of dry air through the flask to displace the remaining CO_2 still present, and to restore the atmosphere in the flask to its original condition. Replace the stoppers and reweigh the apparatus. The loss gives the weight of CO_2 liberated from 1 gram of the salt, for nothing else escapes from the apparatus.

EXAMPLE: Weight of

| | | | |
|---|---|--------|-------|
| apparatus + filter-paper + 1 gram of the salt | = | 77.54 | grams |
| " " " after experiment | = | 77.449 | " |

Loss due to escape of dry CO_2 = 0.205 gram

From the data supplied by Experiments 92 and 93 it is found that 1 gram of blue copper carbonate contains 0.704 gram of CuO , 0.205 gram of CO_2 , and 0.091 gram of H_2O . Then by using the molecular weights, $\text{CuO} = 79$, $\text{CO}_2 = 44$,

$\text{H}_2\text{O} = 18$, the ratio between the oxides in the carbonate can be found and the formula deduced. Thus :

$$\frac{0.704}{79} = 0.0891 ; \frac{0.205}{44} = 0.00465 ; \frac{0.091}{18} = 0.005.$$

By reducing these quotients to the nearest whole numbers the ratio 2 : 1 : 1 is obtained, and the empirical formula of the compound is $2\text{CuO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$, which is thus proved to be a basic carbonate. The composition of the basic carbonates of lead and zinc may be determined in the same way ; but as the commercial compounds are not always pure, only approximate results must be expected.

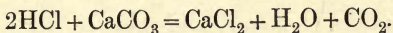
The determination of carbon dioxide in either prepared or natural carbonates may be made with the apparatus used in Exp. 93. Sodium carbonate and marble should be used for preliminary experiments, as they are comparatively pure, and thus furnish a check on the accuracy of the determinations.

CARBON DIOXIDE (CO_2).

It will be useful at this point to examine this important compound a little more closely than has already been done. It is a constituent of the atmosphere, but the quantity present varies somewhat under different conditions. Ten thousand volumes of air contain about 5 volumes of carbon dioxide. It is being constantly passed into the air as one of the products of combustion, respiration, and putrefaction ; and as constantly removed by growing plants, the leaves of which absorb it readily. It is then decomposed under the influence of sunlight, the carbon is assimilated by the growing tissue, and the oxygen is returned to the atmosphere. In this way a kind of rough balance is struck, and the average quantity of carbon dioxide in the air kept about the same.

Preparation of Carbon Dioxide.—If a considerable volume of this gas is required to demonstrate its general properties, it is most readily obtained by dissolving calcium

carbonate in dilute hydrochloric acid. The reaction is as follows :



EXP. 94.—Put some small pieces of clean marble into the bottle A (Fig. 31), and pour in a little water through the thistle funnel B, so as to well cover the solid. Arrange the delivery-tube in the cylinder C, and then add strong hydrochloric acid, a little at a time, through B. A steady stream of gas is thus obtained, which, passing into C, gradually displaces the air and fills the cylinder. It is full when the flame of a burning taper is immediately extinguished on being brought into the mouth of the jar. The gas may also be collected over water.

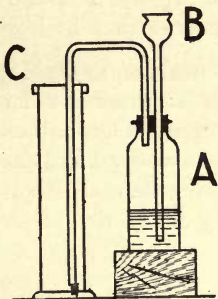
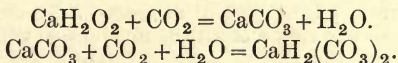


FIG. 31.

Properties of Carbon Dioxide.—

It is a colourless, transparent, odourless gas, and is somewhat soluble in water, which dissolves about 1.5 times its own volume of the gas at ordinary temperatures. The solution has a sour taste, and turns litmus red, thus showing its acid properties. It is non-combustible, and a non-supporter of combustion in the ordinary way; but burning magnesium continues to burn in the gas with formation of magnesia and liberation of carbon. Red-hot charcoal also abstracts oxygen from it. (See Exp. 96.)

Lime-water is turned milky when carbon dioxide is shaken up with it. This is caused by the formation of insoluble calcium carbonate. On further shaking to make the water take up more gas the milkiness disappears, which is due to the conversion of the normal into the soluble acid carbonate. On boiling the solution the normal carbonate is thrown down again. The reactions are shown by the equations :

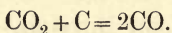


EXP. 95.—Shake up some lime-water in a jar of carbon dioxide

until the solution, which is first turned milky, becomes clear; pour the clear liquid into a test-tube, and boil it.

Carbon dioxide is heavy, and can be poured from one vessel to another in the ordinary way. Its presence in the second vessel is easily proved by putting in a lighted taper, or by the addition of a little lime-water. It is 22 times heavier than hydrogen, and 1.5 times heavier than air.

Carbonic Oxide, CO.—The complete combustion of carbon in air results in the formation of carbon dioxide; but if the supply of air is limited, and the temperature of the carbon is sufficiently high, another oxide of carbon is produced. It is probable that CO_2 is formed first, and then converted into CO by abstraction of part of its oxygen. Thus:

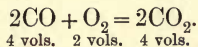


A minimum temperature of about 800°C. , or a bright red heat, is required for the change to go on rapidly. A good table furnace is indispensable. The one shown in Fig. 8 has three Bunsen jets served from one gas tap, and the body consists of a rectangular fire-brick chamber, surmounted by a sheet iron tube to assist the draught. The reaction-tube is a piece of solid-drawn steel tube, such as is used for cycle work, and about 18 inches long. Rubber bungs carry the inlet-tube A and the outlet-tube B, and are kept cool by pads of blotting-paper, which are wrapped round the ends of the steel tube and kept well saturated with water. The charcoal used should be previously heated in a closed clay crucible to the highest temperature of a wind furnace to expel hydrogen and gaseous hydrocarbons, which are not removed during the ordinary process of manufacture. This preliminary heating may be omitted, but then the first two or three jars of gas collected will be impure.

EXP. 96.—Insert a loose plug of asbestos in the steel tube about $\frac{1}{4}$ its length from one end, and fill the middle part with small pieces of charcoal about the size of a pea. Connect the apparatus for generating dry CO_2 , A and B, Fig. 36, with A, Fig. 8, and by the careful addition of dilute nitric acid keep up a moderate stream of

bubbles through the wash-bottle, so as to insure a regular stream of gas through the red-hot tube. If the carbonic oxide is to be quite free from carbon dioxide, a wash-bottle containing a strong solution of caustic soda must be inserted between the end of the steel tube and the collecting cylinder. Collect several jars of the gas.

Properties of CO.—It is a colourless gas with a faint oppressive odour, but must not be inhaled, as it is very poisonous, and should not be allowed to escape unburnt. It burns with a pale blue flame, and explodes when mixed with air or oxygen. The pure gas does not turn lime-water milky, but when it is burnt the product of the combustion does turn the lime water milky, thus proving that carbon dioxide is formed.



CO is only slightly soluble in water. Its density, compared with air = 1, is 0.97.

Experiments with CO.—(1) Add a little lime-water to a jar of the pure gas, and shake the jar; burn the gas and shake the jar again. (2) Mix 1 volume of the gas with 2.5 volumes of air in a tall cylinder, and ignite the mixture. The flame runs rapidly down the jar and thus furnishes an example of incipient explosion. (3) Mix 2 volumes of the gas with 1 volume of oxygen, and ignite the mixture. The combustion is much more rapid, and a decided explosion is the result. The violence of the explosion when an explosive mixture of gases is ignited, depends upon the rapidity with which the combustion extends through the mass.

Formation of CO when a Limited Supply of Air is passed through Red-hot Carbon. EXP. 97.—Disconnect the CO₂ apparatus from the tube used in the last experiment, and replace it by any convenient apparatus for sending a slow stream of dry air through the red-hot charcoal. The form shown in Fig. 32 is very simple. B is full of water; C is full of air; D contains some strong sulphuric acid. By running the water slowly from B into C a slow stream of dry air is forced through the red-hot charcoal, when the drying-bottle D is connected with the tube containing the charcoal. If the issuing gas is required to be free from CO₂, the traces of this gas

can be removed by caustic soda, as described above. Collect two or three jars of the gas. Add some lime-water to a jar of the gas

which has been purified by caustic soda. If the liquid remains clear the gas is free from CO_2 . Put a lighted taper to the mouth of the jar, and when the combustion has ceased, shake up the gas with the lime-water, which turns milky, thus proving the presence of the CO_2 formed by the combustion of the CO. Inflamm another jar of the gas, and notice that it burns with the characteristic blue flame of CO.

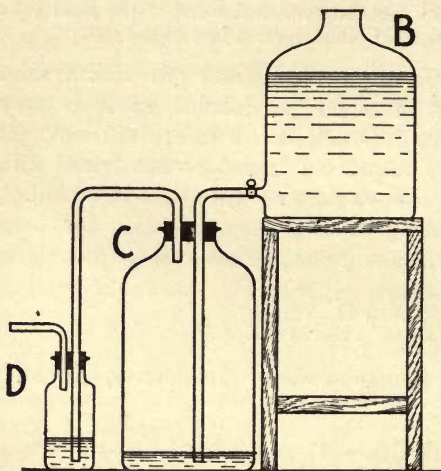
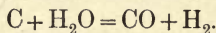


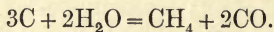
FIG. 32.

The carbonic oxide formed occupies twice the volume of the oxygen absorbed, and is also mixed with the nitrogen of the air from which the oxygen is taken. Thus the mixture contains one-third CO and two-thirds N_2 by volume.

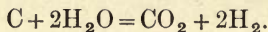
Action of Red-hot Carbon on Water Vapour.—The principal reaction which takes place is one in which carbonic oxide is formed and hydrogen gas liberated.



Another reaction which takes place in a much more limited degree brings about the formation of marsh gas, CH_4 , and probably other hydrocarbons of a similar character.



If the temperature falls too low, hydrogen and carbon dioxide are formed.



So that when steam is passed through red-hot carbon at least three combustible gases are formed. Both reactions are **endothermic**—*i.e.*, more heat is absorbed in effecting the decomposition of the water taking part in the reactions than is evolved by the formation of the resulting compounds when the change takes place; and there is a definite limiting temperature below which it ceases. It is therefore necessary to keep the temperature above this limit by the application of heat from outside, or by allowing some of the carbon to burn to carbon dioxide. Similar remarks apply to the reaction $C + CO_2 = 2CO$, which is also endothermic. On the other hand, $C + O_2 = CO_2$ is an **exothermic** change—*i.e.*, heat is given out while it is taking place.

EXP. 98.—Use the apparatus shown in Fig. 8, but replace the iron by charcoal. Regulate the boiling of the water in the flask so as to give a steady stream of bubbles from the delivery-tube into the collecting cylinder. Collect two or three jars of the gas. It is a mixture of carbonic oxide, hydrogen, and marsh gas, and is called "water" gas. Burn a jar of the gas, and note the faintly luminous flame. Mix 1 volume of the gas with $2\frac{1}{2}$ volumes of air, and explode the mixture. The explosion is louder than with carbonic oxide alone.

Ordinary air contains water vapour, and if it is used in Exp. 97 instead of dry air, a small amount of hydrogen is present in the gaseous mixture obtained.

Coal is a mineral of vegetable origin and of very complex composition. It contains C, H, O, N, and ash-forming constituents. Sulphur is also invariably present in small quantity. The whole of the carbon and part of the hydrogen are available for the development of heat when the coal is burnt. In practice it is usual to subtract from the total hydrogen one-eighth the weight of the oxygen present, and to consider that quantity of hydrogen as already combined in the form of water, and therefore not available for heat production. The remainder is known as available hydrogen. The older the coal the more concentrated it is; for the changes which the vegetable matter undergoes during its extremely slow conver-

sion into coal cause the percentage of carbon, and also the ratio of the hydrogen to the oxygen, to increase. That is, the percentages of oxygen and hydrogen are both decreased, but the former more than the latter.

Coal containing much hydrogen undergoes very complicated changes when it is strongly heated out of contact with air. The greater part of the oxygen is liberated as water; the nitrogen principally in the form of ammonia, and the residue of the hydrogen partly in the free state, and partly in a very numerous and complex series of carbon compounds.

EXP. 99.—Draw off a piece of combustion-tube in the blow-pipe flame; put in it a few grams of powdered coal; draw off and bend the thinned-out portion, as shown in Fig. 33. A is the loaded tube in position; B is a bottle to condense liquid matter; C is a cylinder to collect the escaping gas. Strongly heat the tube as long as gas

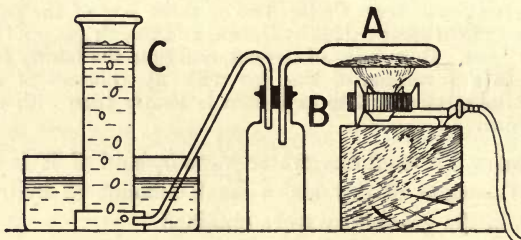


FIG. 33.

collects in C. Remove the cylinder, and put a light to the mouth. The gas burns with a bright white flame. B is found to contain a watery liquid and a black oily liquid. On breaking A, a greyish-black coherent mass of coke is obtained.

The coal is split up into: (1) a combustible gas; (2) a watery liquid which contains ammonia; (3) tar, a liquid of very complex character; (4) coke, a solid residue containing carbon (about 90 per cent.), some hydrogen and oxygen, and inorganic matter or ash.

APPROXIMATE COMPOSITION OF COAL GAS.

| | | | | |
|-----------------------|-----|-----|-----|-------|
| Hydrogen, H_2 | ... | ... | ... | 45 |
| Marsh gas, CH_4 | ... | ... | ... | 40 |
| Carbonic Oxide, CO | ... | ... | ... | 5 |
| Hydrocarbons | ... | ... | ... | 5 |
| Non-combustible gases | ... | ... | ... | 5 |
| | | | | <hr/> |
| | | | | 100 |

The experiment just described illustrates in a general way the principles involved in the manufacture of illuminating gas. If wood is substituted for coal in Exp. 99, a similar result is obtained, and so striking is the analogy that one is forced to admit the similarity in the composition of wood and coal, and the probability that they have the same origin.

The Changes in an Open Coal Fire.—When fresh coal is put on an open fire the heat from the combustion of the fuel already in the grate brings about the changes described above. Water is expelled, and forms the greater part of the first smoke. Then the volatile matter becomes combustible, and burns with a white flame in the current of air passing **over** the fire on its way to the chimney. The coal is gradually coked, and the fire settles down to steady combustion. Another current of air passing **through** the fire by way of the grate-bars gives up its oxygen to the incandescent carbon as soon as it enters, and carbon dioxide is formed. This gas is carried into the heart of the fire, there to be converted into carbonic oxide by the red-hot carbon. On emerging from the upper surface of the fire this carbonic oxide burns with its characteristic blue flame in the stream of air passing over the top. The water vapour in the lower current of air also undergoes similar changes to those already described, hydrogen and carbonic oxide being added to the combustible gas. The earthy matter of the coal is left in the grate as ash. It is evident, from the accumulation of soot in the chimney, and

the contamination of the atmosphere, that combustion in an open grate is far from perfect.

Closed Grate.—If the top of the grate is closed so as to cut off the upper air current, and the bar spaces are arranged to admit a limited supply of air, the combustion is modified, and the gas drawn off from the closed top contains upwards of 30 per cent. of combustible matter. This is known as 'air' gas or 'producer' gas, and is made on the large scale for heating purposes. By introducing more water vapour, up to 10 per cent., gas containing a larger percentage of hydrogen is obtained. The most recent improvements are in this direction.

AVERAGE COMPOSITION OF 'AIR' GAS.

| | | | | |
|---------------------------------|-----|-----|-----|-----|
| Carbonic oxide, CO | ... | ... | ... | 25 |
| Carbon dioxide, CO ₂ | ... | ... | ... | 5 |
| Hydrogen, H ₂ | ... | ... | ... | 10 |
| Nitrogen, N ₂ | ... | ... | ... | 55 |
| Hydrocarbons | ... | ... | ... | 5 |
| | | | | --- |
| | | | | 100 |

The changes are for the most part endothermic, and the complete combustion of a small percentage of the carbon must take place to supply the necessary heat for the endothermic changes.

SUMMARY.

Carbon is found in the free state in Nature. It is also a constituent of many bodies of very diverse composition. It exists in three distinct allotropic modifications. The carbonates are a very important class of metallic compounds, and some of them are used for the extraction of the metals they contain. They are readily decomposed by heat into metallic oxides and carbon dioxide. Acids dissolve them with evolution of the same gas. There are only two oxides of carbon. The dioxide is an acid-forming oxide, and the monoxide is a

very useful combustible gas. Coal and its derivatives, coke and combustible gas, are extensively used in the extraction and after-treatment of the common metals.

QUESTIONS.

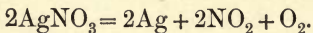
1. Give a short account of the different forms of carbon. How are they proved to be one and the same element?
2. What is the action of heat on carbonates generally?
3. What are the properties of carbon dioxide, and how may it be converted into carbon monoxide?
4. What happens when coal or wood is heated in a closed vessel?
5. Explain fully what takes place when steam is brought into contact with red-hot carbon.
6. Describe the changes taking place in an ordinary coal fire. What is the result of closing the top of the grate? Give the equations expressing the various changes.

CHAPTER XI

REDUCTION

REDUCTION is a term used by metallurgists to express the chemical change which takes place when a metal is set free from its combinations with non-metals. As oxides and sulphides are the most abundant natural compounds of the metals, they furnish frequent examples of reducing action, and are the chief sources of the prepared metals. But for illustrating general principles it will be more convenient to use prepared compounds, and so avoid the complications which would be introduced by the presence of impurities in the natural materials.

Reduction by Heat alone. -- The simplest change is that which takes place when an oxide is decomposed by heat. There are very few examples of this kind of change, for the oxides generally are stable bodies, and not readily decomposed by heat alone. Oxides of mercury, silver, and gold are the only common examples. The decomposition of red oxide of mercury (p. 39) may be taken as typical of the change. But when the compounds are salts of these oxides the decomposition is more complex. Thus with silver nitrate, nitrogen peroxide and oxygen are set free along with the metal.



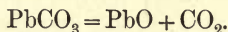
EXP. 100.—Put a crystal of silver nitrate into a small dry test-tube, and heat it in the Bunsen flame. Note the red gas which is given off, and test it with a glowing splint. Remove the reduced silver from the tube, and rub it on a hard surface with the blade of a knife. The particles of the reduced metal are pressed together,

and present the characteristic metallic appearance. The experiment may be made quantitative by weighing the nitrate (about 0.5 gram) before, and the residue of silver after, heating.

A partial reduction is often effected by heat alone, and a simpler compound of the metal thus obtained. This is notably so with the metallic carbonates, of which some examples have been given (p. 169). The decomposition of lead carbonate is easily brought about, but the residue of lead oxide is somewhat readily fused, and, if allowed to get too hot, would spoil a porcelain crucible. Both the normal and the basic carbonates are prepared, and a simple experiment will distinguish between them.

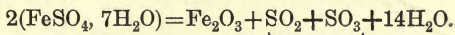
EXP. 101.—Weigh a convenient piece of a broken porcelain dish, and weigh on it 1 gram of lead carbonate. Put the porcelain on a pipeclay triangle and heat it until partial fusion takes place. Allow the porcelain to cool, and reweigh it.

The loss is due to the escape of carbon dioxide, and the result may be compared with the equation—



A partial reduction also takes place when some sulphates are strongly heated, but the reaction is not quite so general as with the carbonates. (See Exp. 86.)

EXP. 102.—Weigh 2 grams of powdered green vitriol in a weighed porcelain crucible, and heat it over a small Bunsen flame for fifteen minutes. Allow the crucible to cool, and reweigh it. The loss is due to the escape of the water of crystallization. Then put the crucible into a gas muffle, and keep it at a moderate red heat for thirty minutes. When the crucible is cold, reweigh it. The second loss is due to the escape of oxides of sulphur. The residue, if not overheated, is a red powder. Compare the results with the equation:

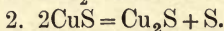
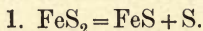


Residue. Second loss. First loss.

This experiment illustrates the method used in the preparation of rouge, and as the colour depends largely on the temperature at which the reduction takes place, care must be exercised in

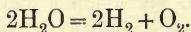
carrying it out. The value of the rouge also depends largely on the grinding and levigation which the residue undergoes after the reduction. (See Exp. 3.)

The partial reduction of metallic sulphides rich in sulphur is demonstrated in Exp. 38. And it may be taken generally that when there are two or more sulphides of the same metal, the one containing the smallest proportion of sulphur is the most stable, and will withstand a high temperature without decomposition. The others are reduced to this stable form when strongly heated. Iron and copper sulphides furnish good examples:

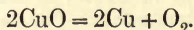


The lower sulphide in each case may be fused at a bright red heat out of contact with air.

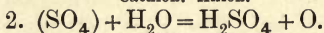
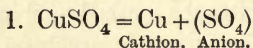
Reduction by Electricity.—The decomposition of water (p. 27) is a simple reduction process as far as the observed effects are concerned. For, though a little sulphuric acid is necessary to the success of the experiment, the final result is expressed thus:



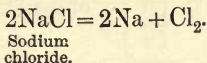
If a solution of copper sulphate is substituted for the acid solution in the voltameter, a deposit of copper is formed on the plate from which the hydrogen escapes during the decomposition of water, and oxygen gas escapes from the other plate. The final result is therefore equivalent to the reduction of copper oxide, whatever the intermediate changes may be.



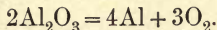
Free sulphuric acid appears in the solution. This is probably due to secondary changes in which water takes part, and furnishes the evolved oxygen:



Similar reactions take place when a current of electricity is passed through a solution of any metallic salt, and if the liberated metal does not act upon water, it is deposited upon the cathode plate (see p. 107). But if the metal reacts with water its hydroxide is formed, and hydrogen is liberated. Common salt fuses to a clear liquid at a red heat, and if a current of electricity is passed through the molten mass between carbon electrodes, the metal sodium and the gas chlorine are liberated and can be readily collected.



Similarly, the cheap production of aluminium depends upon the passage of an electric current through fused cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$, in which alumina is dissolved. The cryolite is unchanged.



Reduction by Heat and Carbon.—Every compound tends to decompose when it is heated, and the higher the temperature to which it is exposed, the greater its proneness to decomposition. Many compounds, however, resist a high temperature, and if their reduction is to be effected the action of heat must be assisted by that of a reducing agent, which may be either an element or another compound. The reducing agent exerts a pull upon one or more constituents of the compound, and thus assists the heat to effect its decomposition. The action is most effective when the reducing agent forms a compound which is volatile at the temperature of the reduction, and is rapidly removed from the sphere of action. But this is not a necessary condition. Carbon, when it helps to reduce a metallic oxide, forms either carbon dioxide or carbon monoxide, according to the temperature necessary to bring about the reduction.

EXP. 103.—Well mix 0.2 gram of powdered charcoal with 8 grams of lead oxide; put the mixture into a small test-tube, and fit the

tube with a bung and delivery-tube, as shown in Fig. 34. Heat the mixture strongly for five minutes, and collect the escaping

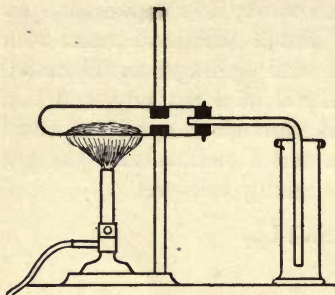


FIG. 34.

gas in the jar. Test the gas with a lighted taper; it is a non-supporter of combustion. Pour the gas from the jar into a beaker containing a little clear lime-water, and shake the beaker; the gas is heavy, and turns lime-water milky. It is carbon dioxide, CO_2 . Examine the residue in the tube for shots of metallic lead.

A similar experiment may be made with black oxide of copper, but the proportion

between the charcoal and the oxide must be nearly three times as great.

EXP. 104.—Put about 2 grams of powdered wood charcoal into a porcelain or platinum crucible; close the crucible with a lid to prevent the admission of air, and heat it strongly over the blow-pipe flame for ten minutes. Allow the crucible to get cold before removing the lid. Charcoal thus strongly heated contains about 92 per cent. of carbon. Weigh 0.054 gram of this charcoal, which is roughly equal to 0.05 gram of carbon. Mix it thoroughly with 4 grams of dry litharge, and introduce the mixture, with the help of a paper gutter, into a piece of combustion tube, $\frac{1}{2}$ inch by 4 inches, closed at one end. Weigh the tube and mixture together; fix the tube in a clip, and heat it strongly in the Bunsen flame until the mixture becomes pasty. Allow the tube to cool, and reweigh it.

The carbon is converted into carbon dioxide by oxygen obtained from the lead oxide, and the excess of the oxide insures the combustion of the whole of the carbon.

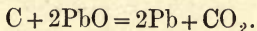
| | | |
|---|---|--------------|
| EXAMPLE.—Weight of tube + mixture | = | 18.983 grams |
| " " after heating | = | 18.799 " |
| | | <hr/> |
| Loss | = | 0.184 gram |

The loss is due to the escape of carbon dioxide containing 0.05 gram of carbon. Therefore the weight of oxygen com-

bined with this weight of carbon is 0.134 gram. These weights may be used to find the formula of the compound.

For $\frac{0.05}{12} = 0.0041$; and $\frac{0.134}{16} = 0.0083$. \therefore The ratio is 1 : 2, and the formula is CO_2 .

Compare the results of the experiment with the equation—



Exp. 105.—Draw off a piece of $\frac{1}{2}$ -inch combustion-tube as shown in Fig. 35. Weigh accurately 3 grams of lead oxide, and transfer it to the tube with the help of a paper gutter.

Weigh the tube and oxide together. Fix it in a clip, and connect the thin end with a rubber tube to the gas-tap. Turn on the gas, and ignite it at the open end of the tube, allowing it to burn with a moderate flame. Heat the tube in the Bunsen flame, and watch the reduction as it proceeds. Note that moisture collects on the cool part of

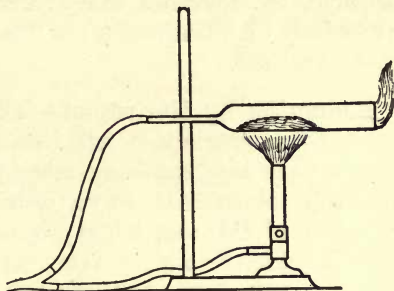


FIG. 35.

the tube at first, but disappears as it gets warm. When the reduction is complete, which is indicated by the disappearance of the oxide, remove the burner, but allow the gas to continue passing through the tube until it has cooled somewhat; then reweigh it.

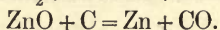
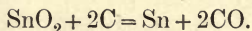
Coal gas contains carbon and hydrogen, and the water formed is the result of the oxidation of the latter (p. 189).

EXAMPLE.—3 grams of lead oxide lost 0.219 gram of oxygen. Then $\frac{0.219}{16} = 0.0137$; and $\frac{2.781}{207} = 0.0134$, so that the ratio is 1 : 1. Therefore the formula of the oxide used is PbO .

An exactly similar experiment can be made with copper oxide.

The temperature required for the above reduction is comparatively low, and carbon dioxide is formed; but when a

high temperature is necessary for the reduction carbonic oxide, CO, is the result. This is not easily demonstrated, and must be left for more advanced work. The reduction of tin and zinc oxides may be cited as examples, and the simplest way of representing the reactions is shown in the equations—



But it is probable that carbon dioxide is first formed, and then reduced by excess of carbon at the high temperature required. Some oxides, such as alumina and lime, require the excessively high temperature of the electric furnace to effect their reduction.

Reduction by Hydrogen.—The action of hydrogen gas upon hot copper oxide has received more attention from eminent chemists than any other experiment in the whole range of the science. It was used by Dumas in his determination of the combining proportion of oxygen, and his experiment has been repeated several times, with every possible refinement of experimental research. For full details of this work some standard book on the subject must be consulted; but a comparatively simple experiment may be described, and even carried out with ordinary care. In this case approximate values only must be expected.

EXPERIMENT TO PROVE THE COMPOSITION OF WATER BY WEIGHT.

The apparatus shown in Fig. 36 is to be fitted up. A is a bottle fitted with a tap funnel, and used for preparing the hydrogen. B is a wash-bottle containing a little water to wash the gas. C is a drying-tube filled with fused calcium chloride and glass-wool. D is a combustion-tube containing ignited copper oxide. E is the water-absorbing portion, which consists of a test-tube, the upper part of which is filled with

glass-wool, and a calcium chloride drying-tube. The delivery-tube from C dips into a small beaker containing a little strong sulphuric acid. This serves to show the rate at which the excess of hydrogen is escaping, and also prevents the absorption of moisture from the air.

To make the experiment, D and E are weighed separately, the rubber joints *a*, *b*, and *c* being closed by the insertion of bits of glass rod. The connections are then made, and a moderate current of hydrogen passed through the apparatus, escaping through the acid in the beaker. When the air has been displaced, the copper oxide in D is heated; the reduction commences, and is continued until a quantity of water has

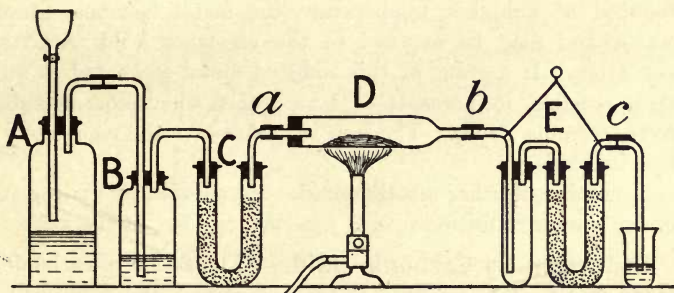
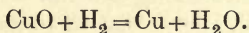


FIG. 36.

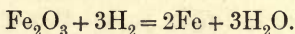
collected in the test-tube of E. The flame is then removed, and the tube allowed to cool with the hydrogen still passing through it. The parts are then separated and reweighed. If the experiment is conducted with care, it proves approximately that the loss of weight in D is to the gain of weight in E as 8 is to 9; or that 8 parts by weight of oxygen combine with 1 part by weight of hydrogen to form 9 parts by weight of water. The reduction is expressed by the equation—



Ferric oxide, Fe_2O_3 , is also readily reduced by hydrogen, and the reaction may be made the subject of a simple experiment.

EXP. 106.—Fit up the apparatus shown in Fig. 36, with the exception of the part E. Put 2 grams of ferric oxide into the tube D, and pass a steady current of hydrogen through it. When the air has been displaced, heat the tube until the red powder turns completely black. Allow the tube to get cold while the gas is still passing through it; then transfer the reduced metal to a dry test-tube and cork it up, to exclude the air from the metal.

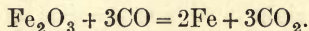
The condensation of water in the cold neck of the combustion-tube is readily observed. The equation is :



If ferric oxide is reduced at as low a temperature as possible, a black pyrophoric powder is obtained, which takes fire spontaneously if allowed to come into contact with the air; but if reduced at a higher temperature the metal is much more stable, and may be exposed to the air when cold without alteration. If a gram of this reduced metal is heated in an open crucible, it increases to 1.43 grams, which corresponds to the formula Fe_2O_3 . The iron is again converted completely into its oxide.

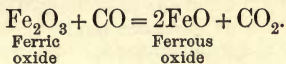
A number of other metallic oxides are reduced by hydrogen under similar conditions.

Reduction by Carbonic Oxide.—The action of carbonic oxide is almost as general as that of carbon and hydrogen. It may therefore be described as a common reducing agent for oxides. The reduction of oxide of iron is very interesting, because the reduced metal reacts on the excess of the reducing gas and absorbs carbon from it. The first change is definite, and is expressed thus :

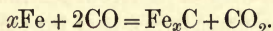


It is found that a considerable excess of carbonic oxide must be used, or the reduction is not complete. The reaction is the principal reducing one taking place in an iron-smelting blast furnace, and it is well known that there must be at least twice as much carbonic oxide as carbon dioxide in the waste gas if the furnace is to work satisfactorily. The general reactions

by which the reducing gas is formed in the blast furnace are described on p. 174; but by using a forced draught a very much higher temperature is obtained in the lower part of the furnace than in a closed grate. For the fusion of the slag and of the reduced metal, as well as the formation of carbonic oxide, has to be considered. A falling off in the proportion of carbonic oxide would result in a partial reduction by which ferrous oxide would be formed, and pass into the slag, with consequent loss of iron. The reaction is:



The second change, in which the reduced metal reacts with carbonic oxide and abstracts carbon from it, is not so definite as the actual reduction of the metal, and is usually considered generally. Thus, if x is used to represent an unknown but determinate quantity, the reaction may be represented thus:



The reactions expressed in the last three equations are readily demonstrated, but the first and third only need be considered here. The carbonic oxide required may be prepared in any convenient way; but the decomposition of yellow prussiate of potash by strong sulphuric acid furnishes a ready means of obtaining the pure gas.

Exp. 107.—Fit up a 2-litre bottle, as shown in Fig. 37, to serve as a simple gas-holder. Put 6 grams of powdered yellow prussiate of potash into an 8 ounce flask, cover it with strong sulphuric acid, and fit the neck with a bung and delivery-tube. Fill the gas-holder with water; connect the flask with the tube A, and gently heat it on gauze over a small flame. Carbonic oxide will be given off steadily if the flask is not heated too rapidly, and will displace the water through the tube B. The quantity of yellow prussiate used should be arranged so that the liberated gas does not quite fill the gas-holder. When the evolution of gas ceases close the tube A with a pinch tap, and the apparatus is ready for use. Draw off a piece of combustion-tube similar to that used in Exp. 105; put into it 2 grams of ferric oxide, and arrange it in a clip for heating over the Bunsen burner. Connect A, Fig. 37, with a drying-bottle contain-

ing a little strong sulphuric acid, and B with the tap of an aspirator filled with water. Place the aspirator on a stand so that its bottom

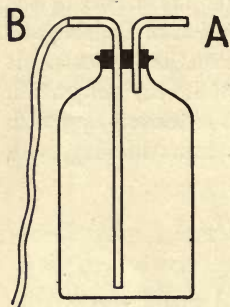


FIG. 37.

is on a level with the tube A. Connect the outlet tube of the drying-bottle with the drawn-off end of the reduction-tube; heat the part of the tube containing the ferric oxide with a Bunsen flame, and drive a steady stream of carbonic oxide over it by opening the tap of the aspirator. The flow of water through B forces the gas through A, and the rate of flow can be easily regulated. Place a Bunsen flame near the outlet of the reduction-tube to burn the excess of carbonic oxide as it escapes. This is most important on account of the very poisonous nature of the gas. When the reduction is complete, fit a cork in the end of the tube to prevent admission of air, and turn off the tap of the aspirator at the

same time. When the reduced metal is cold transfer it to a dry test-tube, and cork it up.

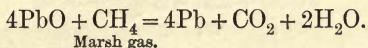
If a weighed quantity of this reduced metal is heated in an open porcelain crucible, it is changed into the red oxide again, but the increase in weight falls considerably short of that obtained in Exp. 106 with the pure metal. This is due to the presence of carbon, which is proved conclusively by the following experiment:

Exp. 108.—Transfer a little of the reduced metal to a combustion-tube; aspirate a current of air over it and through a wash-bottle containing lime-water; heat the part of the tube containing the metal, and note the milky precipitate formed in the lime-water. This proves without doubt that carbon is associated with the iron when it is reduced by carbonic oxide.

Coal gas contains about 5 per cent. of carbonic oxide, and if used for the reduction of ferric oxide the reduced metal contains carbon, but in smaller quantity than when pure carbonic oxide is the reducing agent.

Exp. 109.—Reduce about 2 grams of ferric oxide in the same way that lead oxide is reduced in Exp. 105, and compare the result of heating 1 gram of the reduced metal in a porcelain crucible with the similar results obtained as described above.

The complex character of coal gas makes the individual reactions somewhat numerous when it is used as a reducing agent, but the final result is the same as would be obtained with carbon and hydrogen together. The reaction with the principal hydrocarbon when lead oxide is reduced by coal gas is shown by the equation :

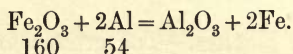
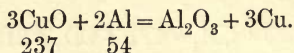


Reduction by Metals.—The great affinity which a particular metal has for an element, or group of elements, in a compound often enables it to replace another metal already in the compound, and so liberate it in the metallic state, when the proper conditions are present. This is the case with aluminium, which exerts a powerful reducing action on some metallic oxides in consequence. The action is accompanied by an extremely rapid evolution of heat, and the local temperature obtained is sufficient to melt the reduced metal, even in the case of such difficultly fusible metals as iron and chromium. Experiments illustrating this mode of reduction are easily carried out. The aluminium used must be in a finely-divided state. Filings, which are readily made from a piece of the rod metal with a moderately coarse file, are suitable for operations on the small scale. The oxides in the form of fine powder should be heated before use to insure their freedom from moisture.

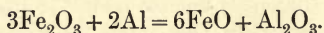
EXP. 110.—Well mix together 10 grams of dry black oxide of copper and 3 grams of aluminium filings; put the mixture into a small clay crucible; make a small cavity in the centre of the mixture with a rod, and into this pour a mixture of 2 grams of barium peroxide and 0.1 gram of aluminium filings. Then insert in this a piece of magnesium ribbon about 2 inches long in an upright position. Place the pot on a brick, ignite the ribbon with a lighted taper, and rapidly replace the lid. When the reaction is finished and the crucible has cooled down, break it and extract the button of metallic copper, which is usually buried in a mass of slag at the bottom of the pot. Repeat the experiment with a mixture of 5 grams of dry ferric oxide and 2 grams of aluminium filings. The

same quantity of the barium peroxide mixture may be used. When the pot has cooled, break it and extract the button of metal.

The change is a comparatively simple one, for it consists of the oxidation of one metal at the expense of the oxygen in the oxide of the other.



A slight excess of aluminium over the quantities found by calculation from the equations is used in the experiments described above, and part of this excess passes into the reduced metal. If in the case of the ferric oxide an excess of that compound is used, the reduction is only partial, and the temperature obtained correspondingly lower. The mixture may be arranged for reduction to ferrous oxide, thus :

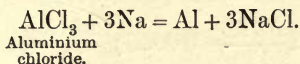


When this mixture is packed round the prepared joint of a steel tube, which is to be hard soldered, and fired, the metal is very rapidly raised to the temperature necessary to melt the solder and make a sound joint.

This method of extracting metals from their oxides is useful in the case of such oxides as those of chromium and manganese, when comparatively small quantities of these metals are required for special purposes. The aluminium used for their reduction must be very finely divided, or the reduction is incomplete.

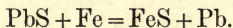
The reducing action of metallic *sodium* when brought into contact with fused chlorides of metals is very marked, and was used for many years in the last stage of the extraction of aluminium on the large scale. But the method has now been superseded by the use of the electric current for the extraction of the metal. The reaction depends upon the

readiness with which sodium combines with chlorine to form common salt. The equation is :

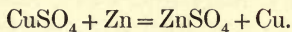


Potassium has similar reducing properties.

Some of the common metals will reduce others from their combinations with sulphur when they are brought into contact with the fused sulphides. The reaction with iron and lead sulphide is a good example of this kind of change ; but the mixture must be raised to a good red heat for effective separation.



Reference should also be made to Exp. 70, and similar experiments in Chap. VIII., as examples of reduction in which the metal is displaced from its combination with a group of elements. The reaction for the separation of copper from copper sulphate by zinc is expressed thus :



Similar reactions are of great importance in a number of metallurgical operations. In such cases the cheapest suitable material is employed. Iron is much used.

Reduction by Potassium Cyanide.—Simple reductions can be brought about by heating some oxides and sulphides with potassium cyanide, KCN, at a moderate temperature. Great care must be taken in handling the cyanide, on account of its highly poisonous nature.

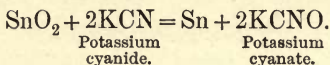
EXP. 111.—Put 3 grams of potassium cyanide into a porcelain crucible, and melt it over a good Bunsen flame. When thoroughly melted, add 1 gram of tin oxide, put on the lid, and continue the heating for fifteen minutes. If the globules of reduced metal have not run together, grip the side of the open crucible with a pair of tongs, and gently shake it over the flame until a single globule of metal is obtained. Pour the liquid contents of the crucible on to a dry porcelain slab, and, when solid, detach the excess of cyanide and weigh the button of metal.

EXAMPLE.—The button of metal from 1 gram of oxide weighed 0.782 gram.

$\therefore 1 - 0.782 = 0.218$ gram of oxygen removed.

Then $\frac{0.782}{118} = 0.0066$; $\frac{0.218}{16} = 0.0136$.

What is the formula of the tin oxide used? (See p. 97)
The experiment by which this result was obtained was made with practically pure tin oxide. The ordinary compound (putty powder) is usually contaminated with oxide of lead, and gives too high a result for the metal. The reaction is thus expressed :

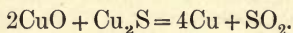


Sulphide of antimony (stibnite) may be reduced in a similar manner; but it is usually too impure to give a good quantitative result. Oxide of lead is also easily reduced by the molten cyanide.

Reduction by Reaction.—This kind of reduction is largely used in the separation of copper and lead from their ores, and is very interesting on that account. It depends upon the fact that if a mixture of compounds, containing the elements of another compound, which can exist in the gaseous state at a temperature below that at which the remaining elements in the mixture are volatilized, is heated, the gas forms and escapes from the mixture. The non-volatile element is left behind in the free state.

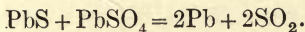
EXP. 112.—Mix together 1 gram of copper oxide, CuO , and 1 gram of copper sulphide, Cu_2S . Put the mixture into a small test-tube, and heat it strongly in the Bunsen flame. Note that sulphur dioxide is given off, and examine the residue when cold for particles of finely divided copper.

The reaction is expressed by the equation :



EXP. 113.—Mix together 1 gram of lead oxide and 1 gram of lead sulphate, and heat as above.

The liberated sulphur dioxide is readily detected by its odour, but the reduced metal is not so easily seen as the copper in the residue from the last experiment. The equation is :



The value of these experiments is in the direct proof they furnish of the formation of sulphur dioxide. In ordinary metallurgical experiments the separation of the metals is taken as an indirect proof of the way in which the reduction is effected.

Reduction Step by Step.—It is possible to reduce some compounds in stages, and thus prove a definite relation between the proportions of two elements in two or more distinct compounds of the same.

EXP 114.—Weigh 2 grams of lead peroxide, PbO_2 ; transfer it to the combustion-tube, Fig. 35, and weigh the whole. Heat the powder until it turns yellow, but do not let it fuse. Allow the tube to cool, and reweigh it. The loss is due to the escape of oxygen expelled by heat. Replace the tube in the clip, connect the end with the gas-tap, and reduce the yellow powder to metallic lead in a stream of coal-gas. When the reduction is finished and the tube is cold reweigh it. The loss is due to the removal of oxygen abstracted by the constituents of the coal gas.

EXAMPLE.—In a carefully worked experiment 2 grams of the peroxide lost 0.133 gram on heating, and 0.129 gram on reduction in coal-gas. Therefore $2 - 0.262 = 1.738$ grams of lead are united with 0.133 and 0.129 gram of oxygen respectively. If these numbers are divided by the atomic weights of the elements to which they belong, the ratio 1 : 1 : 1 is obtained.

This proves that the oxygen is removed in two equal steps, and makes it evident that the second compound may be regarded as formed from the first by the addition of an amount of oxygen strictly proportional to its atomic weight. This is also true of similar series of compounds. Numerous examples might be brought forward, and they would all bear testimony in the same direction. The following are examples of such series: CO , CO_2 ; Cu_2O , CuO ; CrO , Cr_2O_3 , CrO_3 .

The generalization based upon these facts is known as the law of chemical combination in multiple proportion (see p. 52).

The series of compounds included in this generalization, which, it must be remembered, is based entirely upon experimental evidence, and is therefore a statement of facts, afford very strong support to the atomic theory. For it is perfectly clear that after a particular compound has been formed, a second addition of one of its elements may take place, by which another equally definite compound is produced. Further, the amount of the added element is strictly proportional to its atomic weight, for the second compound is formed by a distinct jump from one proportion to the other. It is, then, easy to imagine that the molecules of the higher compound are formed by the addition of invariable particles or atoms of the element to the molecules of the lower compound.

SUMMARY.

Reduction is one of the most important operations in metallurgical work. The selling price of a metal depends largely upon the readiness with which it is reduced from its ores. The reduction of a metallic compound may be complete, and the metal set free; or it may be only partial, and a lower compound of the metal obtained. Only a few metals are liberated from their compounds by heat alone. Assistance has to be rendered by reducing agents, of which carbon, carbonic oxide, and hydrogen are the most important for the reduction of metallic oxides. The formation of carbon dioxide and water is easily proved. The electric current is coming more and more into prominence as a reducing agent, and it is in use on the large scale for the extraction of several metals. Metals themselves are not quite so prominent in the list of reducing agents as they were, but iron, copper, and zinc are still largely used in the metallurgy of gold and silver. Potassium cyanide is only used on the

small scale for the reduction of metals from oxides and sulphides. Step-by-step reduction, and its bearing on the second law of chemical combination, is of great theoretical importance.

QUESTIONS.

1. What do you understand by the partial and complete reduction of a compound? Give examples.
2. How may a reduction experiment be used to determine the formula of an oxide?
3. Describe an experiment by which the composition of water is determined.
4. What is the composition of coal gas? Write out equations showing the effect of its various constituents upon a heated metallic oxide.
5. Write down the law of chemical combination in multiple proportions. What is the nature of the support it lends to the atomic theory?
6. How is sulphur dioxide formed in a reduction process

CHAPTER XII

COMBUSTION

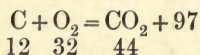
IN Chap. XI. some experiments are described in which metals are reduced from their oxides by carbon and hydrogen respectively; and it is proved that carbon dioxide and water are formed in the reactions which take place. From this it is evident that metallic oxides can act as oxidizing agents, and in doing so give up their oxygen to the bodies by which they are reduced to the metallic state. But in order that these changes may take place, it is necessary to heat the metallic oxides in contact with the reducing agents above certain limiting temperatures, below which no action is observed. The reason for this is that the affinity of the oxygen for the metal must be overcome before the carbon or hydrogen can combine with it. The effect of the decomposing action of the heat on the oxide, and the pull of the reducing agent upon its oxygen, bring about the decomposition, when they are together greater than the attraction of the elements in the oxide for each other. Then the reducing agents burn in the oxygen of the oxides.

When carbon and hydrogen oxidize freely, and the action continues without the aid of external heat, the change is commonly known as combustion: but the compounds formed are the same as in the reduction of oxides. The heat developed in their formation is, however, much greater than that used up in rendering the changes possible, and so the action continues as long as the necessary materials are supplied.

There is a certain limiting temperature for a given com-

combustible body, below which it may be exposed to the air without taking fire. This temperature is called the **ignition point**, and varies for different bodies. If the body is exposed to the air at this temperature, or a little above it, oxidation commences, heat is developed, and a further rise in temperature takes place. This increases the action, and if the body burns freely its maximum rate of combustion is soon reached, and continues steadily as long as the conditions are constant. The rate of combustion must depend upon the rate at which the particles of oxygen are brought into contact with the combustible body. Also, the local temperature depends largely upon the rate of combustion, and this can be increased by bringing more particles of oxygen into contact with the burning body in a given time. This is commonly effected by blowing, and the higher temperature obtained by burning the combustible body in a rapid current of air is explained. A further increase in the temperature takes place if the air is heated before it comes into contact with the burning body; for the heat which would be used up in raising the products of combustion and the residual nitrogen to the temperature of the heated air, is now available for increasing the general temperature.

It has been already stated that the quantity of heat liberated during a chemical combination is just as definite as the quantity of the compound formed. Thus the thermo-chemical equation



means that 12 grams of carbon in burning completely to carbon dioxide liberates sufficient heat to raise 97 kilograms of water through 1° C. Similar thermal equations may be written for other combustible bodies.

Further, it must be carefully noted that exactly the same quantity of heat disappears if the compound formed during combustion is decomposed into its elements again. And it is also certain that there is a limiting temperature at which the

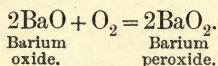
compound is decomposed as fast as it is formed. This higher limit is the temperature of dissociation of the compound, and is the theoretical limit to the temperature obtained by the combustion of the element forming the compound. The practical limit, which is influenced by a variety of circumstances, seldom reaches this. Some assistance in understanding this limit may be obtained by considering the experiment with mercury, described on p. 17. Here it is evident that a certain minimum temperature is necessary in order that the mercury may oxidize; but, if the oxide is exposed to a temperature not much higher than that at which it is formed, decomposition sets in, and the elements are reproduced. It is, then, certain that there is a temperature at which the oxide is decomposed as fast as it is formed, and that above this limit no permanent oxidation is possible. Thus, however favourable the conditions may be under which a body is burnt, there is a limit to the temperature of the products of its combustion. When air is used for burning a body, every molecule of oxygen brought into contact with it has four molecules of nitrogen in its train. Now, if these are replaced by oxygen molecules, it is evident that a more rapid action must result. This is what happens when pure oxygen is used in place of air: it has the same general effect as a rapid current of air, without the disadvantage of the presence of a considerable body of nitrogen to absorb heat, and thus to lower the general temperature. If, then, pure oxygen is used to surround the burning body instead of air, the effect should be considerably increased. This may be rendered perfectly clear by making a few experiments with oxygen itself.

OXYGEN.

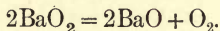
Preparation of Oxygen from Air (Brin's process).—This commercial process depends upon the fact that when barium oxide, BaO , is heated to a certain temperature in a current of air, it absorbs oxygen rapidly, and is converted into

the peroxide, BaO_2 , and that when this compound is heated to a still higher temperature, it is decomposed into the lower oxide again, oxygen being set free. It is another case of a limiting temperature, above which the change is reversed. But it is found that by reducing the pressure over the hot peroxide the limiting temperature for decomposition may be brought down to that at which absorption of oxygen takes place under ordinary pressure. By taking advantage of this the process is made an alternating one, by varying the pressure instead of the temperature, which is much more convenient.

Barium oxide is heated in iron tubes arranged in a furnace, and a current of air, freed from carbon dioxide and water by passing it through vessels containing caustic soda and lime, is passed over it. Absorption takes place :



The air current is then stopped, and the tubes carefully exhausted by a pump, when, without interfering with the temperature of the tubes, oxygen gas is liberated.



The first portion of the gas is allowed to escape, as it is contaminated with the nitrogen present in the tubes when the air is cut off; the remainder, which is pure oxygen, is passed into a gas-holder as fast as it is liberated. The oxygen thus obtained is forced in large quantities into strong portable iron bottles, from which it can be drawn at will. The gas stored in this way is very convenient for use at short intervals.

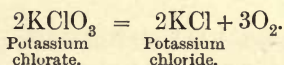
Preparation of Oxygen from Potassium Chlorate.

—When small quantities of the gas are required at irregular intervals, it is better to prepare it as required.

Exp. 115. — Mix 10 to 20 grams of powdered potassium chlorate with a quarter its weight of black oxide of manganese, and put the mixture into a test-tube, 1 inch wide and 7 inches long, fitted with a bung and

delivery-tube. Arrange the tube in a horizontal position, as shown on p. 39, so that there is a clear channel between the mixture and the side of the tube, and with the free end of the mixture not too near the bung. Heat the tube carefully, beginning at the free end of the mixture, and gradually carry the flame along as the escape of gas slows down. Collect several jars of the gas, and one stoppered bell jar of about 1,500 c.c. capacity.

One gram of the chlorate liberates about 270 c.c. of oxygen, so that a rough calculation can be made for the quantity required, and waste thus avoided. The change is given by the equation :



The black oxide undergoes very little change itself, but assists the oxygen to escape at a lower temperature than when the chlorate is used alone.

Properties of Oxygen.—It is a colourless, odourless, and tasteless gas; only slightly soluble in water, and the most important supporter of combustion. The following experiments may be made with the gas prepared as above :

1. When a glowing splint is put into the gas it is rekindled.
2. When a piece of good charcoal is made red hot in the Bunsen flame, and then plunged into the gas, it burns vigorously, emitting much heat and light, but without flame. The residual gas turns lime-water milky; it is carbon dioxide.
3. Sulphur when feebly ignited bursts into more vigorous combustion, and burns with a violet flame. The residual gas has the odour of burning sulphur, and turns litmus red. It is the acid-forming sulphur dioxide.
4. When ignited phosphorus is put into oxygen it burns with a very bright flame. The acid oxide P_2O_5 is formed. A common jar should be used for this experiment, as it is liable to fracture from the great heat developed.
5. A piece of thin steel ribbon made into a spiral, and one end tipped with a short piece of a wax match, burns very vividly when the wax is ignited and the whole put into a

bell-jar filled with oxygen, and standing over water. See Fig. 38.

6. If two small candles supported in deflagrating spoons are ignited and put into two cylinders, one containing air and the other oxygen, a very marked difference is observed in both the rate of combustion and the appearance of the flames. In the air the candle burns at the normal rate for a short time, then the flame languishes, and finally disappears. In the oxygen the flame shrinks, becomes much brighter, and the rate of combustion is increased. An

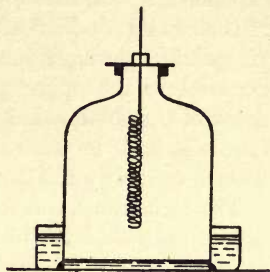


FIG. 38.

increase in temperature is evident from the fact that the wax melts, and runs down into the spoon. The flame finally disappears. The formation of carbon dioxide during the combustion is easily proved by pouring a little clear lime-water into each jar; on shaking, the lime-water is turned milky.

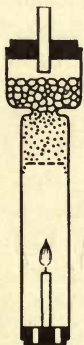


FIG. 39.

Combustion in Air and other Bodies.—The burning of a candle may be made the subject of an experiment by which the increase in weight due to the combination of oxygen with the constituents of the combustible body may be proved. A lamp chimney, Fig. 39, is divided into two parts by a piece of wire gauze. The upper part is filled with a mixture of caustic soda and calcium chloride in small lumps, and the upper end is fitted with a perforated cork. Another perforated cork bearing a small candle is inserted in the lower end. The whole is then hung by a wire loop on to the end of the scale-beam of a balance from which the scale-pan has been removed, and counterpoised. The lower cork is then removed, the candle ignited,

and rapidly returned to the tube. Very soon the apparatus begins to show an increase in weight, although the candle is actually disappearing. The cause of this increase is readily explained, if it is borne in mind that the carbon and hydrogen of the candle combine with and thus abstract oxygen from the air passing through the apparatus, and that the absorbing material in the upper part prevents the escape of the products of the combustion. Thus the whole of the matter of the candle is kept in the tube, together with the added oxygen. This is evidently the cause of the increase in weight.

The formation of water during the combustion of hydrogen, or combustible bodies containing hydrogen, is easily demonstrated. The drying-tube of the part of the apparatus for generating dry hydrogen is fitted with a piece of clay tobacco-pipe, and the long tube passing into the wash-bottle is raised just above the surface of the liquid (p. 189). The apparatus shown in Fig. 19 is carefully dried, and the head of the thistle funnel arranged over the clay jet, the angle-tube being connected with an aspirator. The jet of hydrogen is then ignited, and a current of air aspirated through the thistle funnel. Very soon water appears in the bottle, and the only explanation of its presence there is that it has been formed by the burning of the hydrogen in air. A jet of coal gas or a burning candle may be placed under the funnel with a similar result.

Combustion is not limited to air or oxygen, for hydrogen, combustible bodies containing hydrogen, and finely divided metals burn readily in chlorine (p. 74). Nitrous oxide and nitric peroxide are also supporters of combustion. Finely divided metals will also burn in sulphur vapour.

EXP. 116.—Put some sulphur into a wide test-tube; fix the tube in an upright position, and strongly heat it. When the sulphur is boiling vigorously lower a spiral of thin copper ribbon into the vapour. In a short time it becomes red hot, due to the rapid sulphidation. The metal burns in the sulphur vapour. When the spiral is withdrawn it is found to be changed into copper sulphide.

Explosive Combustion.—In ordinary combustion the

conditions are such that the burning body and the supporter of combustion are supplied to each other steadily, and any alteration in the rate of supply alters the rate at which the action takes place. Explosion of a mixture of gases or solids is simply rapid combustion, and takes place when the two bodies are so intimately mixed that the entire action is spread over a very short space of time.

The explosion of a mixture of coal gas and air is a familiar example, and the energy of the change is unmistakable. The working of an ordinary gas engine depends upon a series of such explosions. Gunpowder is an example of an explosive mixture of solids; it is a case of the rapid oxidation of carbon and sulphur by the oxygen obtained from the saltpetre. A large quantity of gaseous matter is thus formed in a limited space, and the enormous pressure which this gas is able to exert easily accounts for the effects produced.

Inversion of Combustion.—The terms combustible and supporter of combustion are merely relative. In the ordinary way we say that coal gas burns in air; but it is easy to invert this order of things, and make the air burn in coal gas. A very simple experiment will prove this.

EXP. 117.—Fix a lamp chimney in a clip, insert a cork, through which two tubes pass, as shown in Fig. 40, in the bottom, and put a gauze cap on the top. Connect the angle-tube *a* with the gas-tap, and ignite the jet of gas escaping through the gauze. Tip the end of a thin splint of wood with a fragment of phosphorus, ignite it, pass the splint rapidly up the straight tube *b*, and ignite the jet of air at the top.

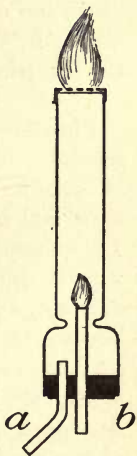


FIG. 40.

The direct ignition of the jet of air as described, although more convincing, is not always easy to bring about. Another way is to close the top of the chimney with a cork, through which a glass tube is passed, to turn on the gas freely, and

to ignite it at both top and bottom tubes. If then the supply is regulated carefully, the flame at the end of the bottom tube will strike back up the tube, and appear at the inner end as a jet of air burning in coal gas.

The current of coal gas passing in through *a* and up the chimney draws in a current of air through *b*, so that a jet of air is supplied to an atmosphere of coal gas. The air takes fire and burns with a flame, which, though not so luminous as the flame of coal gas burning in air, resembles it in general appearance.

Similarly, oxygen may be burnt in hydrogen, and chlorine in hydrogen. It can then be said that when two gases are concerned in the act of burning either may be supplied in a jet to the other as a supporting atmosphere. But the chemical change is the same whichever way the action takes place. Thus, for oxygen and hydrogen water is the invariable product. If, however, one of the bodies is a non-volatile solid, the inversion is not possible.

Flame.—The burning of carbon and sulphur in oxygen furnishes examples of combustion in which a marked difference is noticed. The carbon becomes incandescent, and gives out light and heat, but without flame. It is a non-volatile solid. The sulphur, on the other hand, gets hot and vaporizes. This vapour diffuses, penetrates the surrounding space for some distance, and burns there. The space in which the vapour burns is filled with flame, and in the whole of this region the combustion is going on. In the first case the zone of combustion is confined to the surface of the burning solid, and the heat developed is concentrated in space. In the second the zone of combustion is extended to the region about the burning body, and the heat is distributed over a larger space.

The appearance of the space in which gaseous matter is burning gives the general idea of flame, and the further the vapour penetrates into the space before it is completely burnt the larger will be the volume of the flame. Bearing this in

mind it is easy to explain why a candle flame shrinks when it is fed with pure oxygen. For the oxygen burns up the combustible gases emanating from the wick of the candle before they have time to penetrate very far into the surrounding space, and a shrinking of the zone of combustion takes place. The local temperature is increased by this, and also by the more rapid burning. If it is required to localize the heat so as to attain a high temperature in a small space, a combustible body which preserves its solid state during the whole period of its combustion should be used, and the gas in which it is burnt should be supplied as fast as possible. On the other hand, when it is necessary to spread out the heat, so to speak, through a larger space, gaseous fuel must be used. Also, the supply of air must be such as to allow of perfect combustion in as large a region as possible. Charcoal, coke, and anthracite are examples of fuel which, when burnt in a good supply of air, give high local temperatures. But gas coal, or long flaming coal, which contains a large percentage of volatile combustible matter, is more suitable for the distribution of heat. Gaseous fuel, however, may be used for obtaining a high local temperature, if it is suitably burnt. The shrinking of a candle flame in oxygen suggests the means to be adopted; and the oxy-hydrogen blow-pipe flame is an excellent example of its application. The tendency to do away with the use of solid fuel for all purposes to which combustible gas can be applied is growing; and the use of gaseous fuel may be regarded as a distinct scientific, economic, and hygienic advance upon the dirty, wasteful methods of heat production still so largely used. Producer gas, water gas, and Mond gas are now quite familiar terms.

The Structure of Flame.—The complexity of a given flame varies with the constituents of the gas producing it, and the conditions under which the gas is burnt. A general idea, however, can be obtained by a few simple observations. If the air-way of a Bunsen burner is stopped a luminous flame is

obtained at the top ; and if the gas is turned down so as to give a small flame without flickering, the flame is seen to consist of three parts : (1) a blue portion, appearing to spring from the top of the burner ; (2) a luminous portion, which occupies the upper part of the body of the flame ; (3) a faintly-luminous mantle, which surrounds the whole body of the flame and forms its limits. A dark portion, which does not belong to the flame proper, is noticed in the lower part, and this region is filled with unburnt gas. This is easily proved by thrusting the head of a match rapidly through the envelope into this space, and the fact that it does not ignite there is sufficient evidence that combustion is not taking place in that space. These observations are most successful in an otherwise dark room. An ordinary candle flame has an exactly similar appearance. The same conical space filled with unburnt gas is present in the ordinary Bunsen flame, and its presence may be demonstrated by holding a piece of stiff white paper well down on the flame for a second or two, so as to cut through this space. A black ring surrounding a white centre shows where the paper has been in contact with burning and non-burning gas.

The **Luminosity** of flame is of considerable importance when it is a question of obtaining as much light as possible from the burning gas. The white flame, which is so much prized in illuminating gas, is not due to any single cause. It is probably largely caused by the presence in that portion of the flame of dense gases and solid particles, produced by complex changes in the gas before its complete combustion. An increase in the pressure under which a gas is burnt also increases the luminosity of its flame, but this condition is not commonly present to any extent. The hydrogen flame gives out very little light, which is due to the extremely simple character of its combustion ; but if fine particles of solid matter are passed into it its luminosity is at once increased. This principle is adopted in converting the practically lightless

flame of a Bunsen burner into a brilliant one by suspending in it a mantle made of a very light infusible oxide, which is rendered incandescent by the heat of the flame. The burning of phosphorus, on the other hand, proves that it is possible to have a highly luminous flame without the presence of solid particles in it. For solid matter cannot possibly be present in this flame. Also, the highly-luminous flame of burning acetylene, C_2H_2 , is probably largely due to the endothermic character of the compound itself. Much heat is absorbed in its formation, and this heat, which is liberated during its decomposition, is added to that evolved by the combustion of its constituents. A very high local temperature is thus obtained with the other conditions for a luminous flame.

THE ENERGY OF COMBUSTION.

The Conservation of Energy.—Since combustion is the principal source of artificial heat, if it may be so called to distinguish it from the natural heat derived from the sun, it will be in place here to inquire a little into the nature of heat. In the first place, heat is real, but it is not ponderable ; that is, it lacks the intrinsic property of matter, which is best denoted by substance or density. It has been defined as a mode of motion ; but as we can form no idea of motion without something to move, it does not appeal to us until it is associated with bodies of some kind. Heat motion in bodies is a movement of their *particles*, and not of the bodies as a whole. A full discussion of the nature of heat will be found in books on the subject ; but, for our present purpose, it is sufficient to recognise its ability to cause an increase in molecular motion when it enters bodies, and a decrease in that motion when it leaves them.

When a body is moving it is said to possess **energy**, for it is capable of doing work. This kind of energy is **kinetic** or “moving” energy. Therefore, since we have no experience of absolutely cold bodies, such bodies as we know

possess a store of this moving energy, due to their molecular motion.

But bodies may also possess energy due to their position with respect to other bodies. Thus, they may be able to fall and, in falling, to do work. This kind of energy is **potential**, or "stored" energy. The potential energy of a body appeals very strongly to the mind at times. If one is looking up at a piece of overhanging rock on the top of a cliff, the feeling will arise as to what would happen if it were to fall. The same piece of rock lying at one's feet does not create the same impression. When a body is falling its potential energy, which depends upon its position, is being rapidly converted into kinetic energy, and just before it reaches the surface towards which it is falling, all the potential energy due to its original position with respect to that surface is converted into moving energy. By impact with the surface the body is brought to rest, and it would appear as if its energy of motion were destroyed; also, since it no longer possesses the potential energy due to its former position, that a complete disappearance of energy had taken place. But further examination proves that the energy of motion of the mass is not destroyed; it is converted into increased motion of the particles of the body and the surface struck by it. That is, it is converted into heat. Further, the heat energy developed is exactly equivalent to the kinetic energy lost. The same reasoning holds for every modification of energy. This principle, which is known as the **conservation of energy**, has been most exhaustively studied in connection with the relation between heat and mechanical work, and in the case of these two modifications of energy has been proved up to the hilt. Those who are most qualified to give an opinion hold that the same is true for every other modification of energy.

Every particle of matter has energy associated with it, and when a redistribution of the particles of a body, or system of bodies, takes place, there is also a redistribution of the energy associated with them. The energy of chemical attraction is of

the potential kind, and when the conditions are such that this attraction is able to bring about chemical change in the matter of the reacting bodies, a change in energy also usually results. Take, for example, the case of a mixture of oxygen and hydrogen: the two gases are ready to combine with each other, and a considerable amount of energy is stored up in their molecules. When the mixture is exploded a redistribution of the atoms of the gases to form molecules of water takes place, and this is accompanied by rapid conversion of the potential energy of chemical attraction into the kinetic energy of the heat evolved. The cause of the force exerted between dissimilar bodies when chemical changes are affected, and the nature of chemical energy, are quite unknown, but this does not prevent us from using ideas suggested by the results. The conversion of chemical energy into heat resembles very much the conversion of the energy of a falling body into heat when it is brought to rest by collision with the earth; and it does not appear at all improbable that the change in the motion of the atoms of oxygen and hydrogen in their endeavour to form new and more stable molecules is the cause of the conversion of the stored chemical energy into heat. The action going on when a piece of red-hot charcoal is surrounded by oxygen or air may be pictured in the same way. The atoms of oxygen become associated with the atoms of carbon, and form molecules of carbon dioxide, and the transformation of energy goes on vigorously. During the rush and turmoil of the action, chemical energy disappears, and heat energy appears in the same proportion.

No difficulty should now be experienced in explaining the fact that different modifications of carbon appear to give out different quantities of heat when they are completely burnt. The different forms of carbon are admittedly due to a different arrangement of the molecules or atoms of the element, and not to a difference in the quality of the atoms themselves. It is, therefore, quite feasible that the atoms of carbon in graphite require more to bring them up to the condition necessary for

union with oxygen than do the similar atoms of carbon in charcoal, and that the energy required to do this work of preparation is subtracted from the total quantity of heat, which would be developed by the burning of the free atoms of carbon. In fact, it is analogous to the case of a body which has to be lifted into a position from which it can fall. Here the energy used up in lifting the body into position is to be subtracted from the total heat developed by the impact of the body when it is brought to rest. It may, then, be said that the distribution of energy in the allotropic modifications of carbon is not the same. This holds for sulphur too; for the monoclinic form of that element evolves heat when its crystals pass into the more stable rhombohedrons (p. 57). Generally, when an element passes from a more stable to a less stable form, heat is absorbed, but heat is evolved in the opposite change. When a group of molecules of different bodies are reacting among themselves, and forming molecules of a new body or bodies, evolution or absorption of heat takes place according as the new molecules are more or less stable than the reacting molecules. When heat is **evolved** the change is **exothermic**, and when it is **absorbed** the change is **endothermic**. All the common combustion processes are exothermic in character; and a number of changes will be met with in metallurgical operations, which are distinctly endothermic in character. They do not take place unless heat is supplied from without. Energy then, as we know it, is a condition of matter, and like matter can undergo a variety of changes, and, in any self-contained system of bodies, the amount of energy, like the amount of matter, is absolutely fixed.

MEASUREMENT OF HEAT.

When a given quantity of heat enters a body and distributes itself uniformly through the substance of the body, a change takes place in its thermal properties, and the temperature of the body is said to rise. This change of temperature depends

upon (*a*) the mass of matter in the body, and (*b*) its power of absorbing heat. The latter property is termed its specific heat, and is dependent upon the kind of matter concerned in the absorption. Specific heat and temperature are regarded as the two factors of heat energy, and are measured by reference to arbitrary standards. The temperature of a body indicates the intensity of its heat energy, and is the factor which determines the possibility of heat entering or leaving the body under given conditions. Thus if two bodies at different temperatures are brought together, heat will pass from the body at the higher to the body at the lower temperature, and the exchange will go on until the intensity of the heat energy is the same in both. The temperature of the one body rises and that of the other falls, until it is the same for both. But the quantity of heat which leaves the one body and enters the other also depends upon their specific heats—*i.e.*, upon the other factor of heat energy. Thus if a number of bodies at different temperatures are brought together and left to themselves, exchange of heat energy will take place between them, and they will finally reach one dead level of temperature, the value of which will depend upon the masses, specific heats, and temperatures of all the bodies in the system. It is assumed in this general statement that no process other than redistribution of heat energy takes place in the system.

Measurement of Temperature.—Advantage is taken of the fact that bodies in general expand when heated and contract when cooled, and that this expansion and contraction may within certain limits be taken as a measure of the rise and fall of their temperature, and, therefore, of that of other bodies with which they are in contact. The instruments used for registering moderate temperatures are called thermometers, and those for high temperatures pyrometers. The mercurial thermometer consists of a glass bulb and tube nearly filled with mercury. The relation between the capacity of the bulb and the diameter of the bore is such that the metal does not

quite leave the bore at the lowest, and does not quite fill it at the highest temperature the instrument is intended to register. The fixed points of the scale are obtained by first immersing the instrument in melting ice, and then in the steam from water boiling at normal pressure. The point on the stem to which the mercury recedes when exposed to the temperature of melting ice is marked as the freezing-point of water, for ice melts and water freezes at the same constant temperature; the point on the stem to which the metal expands when exposed to the steam is marked as the boiling-point of water, for the steam from water boiling at a constant pressure has a constant temperature. The space between these points is divided into degrees, which are marked on the scale.

On the *Centigrade* scale there are 100° between the freezing and boiling points. Thus the freezing-point is marked 0° C., and the boiling-point 100° C. The scale may, however, be graduated above and below these points; the lower limit is the freezing-point (-39° C.), and the upper limit the boiling-point (350° C.) of the mercury itself. But when the temperature of the metal approaches either of these limits the indications are uncertain, and it may be said generally that the rate of expansion of a body is not strictly proportional to its increase in temperature, and the hotter it gets the greater is its deviation, so that in accurate instruments corrections have to be made for this deviation. In the case of mercury the deviation is small between 0° and 100° , and can be corrected for at higher temperatures, so that some mercurial thermometers are constructed to register upwards of 300° C.

The temperature scale commonly used in the British Isles is the *Fahrenheit*, on which the freezing-point is marked 32° , and the boiling-point 212° , thus giving 180° between the two points. The conversion of a reading on the Fahrenheit scale to the corresponding reading on the Centigrade is easily effected, for $\frac{F}{C} = \frac{180}{100} = \frac{9}{5}$; therefore $F = \frac{9}{5} C$, and $C = \frac{5}{9} F$; but in converting F. into C. the 32° below the freezing-point must

be subtracted before, and in the conversion of C. into F., added after, the calculation is effected. This is given by the expressions :

$$C = (F - 32) \frac{5}{9}; F = \frac{9}{5} C + 32.$$

To determine the temperature of a given body, the thermometer is brought into contact with it, the two allowed to come into equilibrium, and the reading then taken. The mass of the thermometer is kept as small as possible, so that the quantity of heat entering or leaving it while coming into equilibrium with the body may not sensibly interfere with the temperature to be measured.

The construction of *pyrometers* for the measurement of high temperatures is based upon various principles, such as the expansion of solids and gases; the increase in the electrical resistance of a metal wire when heated; the current generated by a thermo-electric junction when its temperature is increased, etc.; but standard works on metallurgy, heat, and electricity must be consulted for a description of such instruments.

Specific Heat.—It is a matter of common experience that different weights of the same substance at a given temperature absorb or give out different quantities of heat when they are raised or lowered through the same range of temperature, and that these quantities are strictly proportional to the masses of the substance under consideration. Thus, 2 pounds of water at 50° C. would liberate twice as much heat in falling to 20° C. as 1 pound would under the same conditions. Now, if the heat given out by a given weight of water in cooling through a given range of temperature is absorbed by a given weight of iron, it is found that 3.57 times that weight of lead is required to absorb the same quantity of heat; or a quantity of heat which would raise 100 grams of iron through, say, 10° C. would raise 357 grams of lead through the same temperature. This difference in the absorbing power of the two metals is said to be due to the difference in their specific heats. The

heat-absorbing power of water is greater than that of any other compound or element, and is taken as the standard. The specific heat of water = 1, so that the specific heats of all other pure substances is less than unity when compared with this standard.

The method of determining the specific heats of solid bodies such as metals may be thus described: A known weight of water, W , is placed in a vessel called a calorimeter, and its temperature, T° , taken; a known weight of the body w , which has been raised to a temperature, t° , is then immersed in the water and moved about until the two come to the same temperature, and the temperature of the water, T_1° , again taken. Now, while the temperature of the water rises from T° to T_1° , the temperature of the body falls from t° to T_1° , and the heat given out by the body is equal to that absorbed by the water; but the quantity of heat given out by the body is proportional to its mass, specific heat, and fall in temperature, and the quantity absorbed by the water to the same factors; but these quantities of heat are equal, therefore

$$(t^\circ - T_1^\circ) \times w \times s = (T_1^\circ - T^\circ) \times W \times S,$$

where s and S are the specific heats of the body and water. But as $S = 1$ —*i.e.*, the specific heat of water— s , the specific heat of the body, is the only unknown quantity, and its value is easily found from the equation.

EXAMPLE.—A lump of platinum weighing 2 ounces is raised to a temperature of 410°C. , and is then plunged into 20 ounces of water at 16°C. ; the resulting temperature of the water is found to be 17.3°C. What is the specific heat of platinum?

$$t^\circ - T_1^\circ = 410 - 17.3 = 392.7, \text{ and } T_1^\circ - T^\circ = 17.3 - 16 = 1.3.$$

$$\therefore 392.7 \times 2 \times s = 1.3 \times 20 \times 1;$$

$$\text{or } s = \frac{1.3 \times 20}{392.7 \times 2} = 0.033.$$

A correction has to be made for the heat absorbed by the calorimeter, but this and other points in connection with the accurate determination of specific heats cannot be discussed here. The specific heat of platinum between 0°C. and 100°C.

is 0.0323, and increases slightly at higher temperatures. The definite relation between the specific heats and atomic weights of metals is discussed on p. 128.

The unit of heat quantity is the calorie, which is the amount of heat required to raise the temperature of 1 gram of water from 0°C. to 1°C. The great calorie or kilogram unit, which is equal to 1,000 calories, is often used for practical work; also the quantity of heat required to raise 1 pound of water from 32°F. to 33°F. , or from 0°C. to 1°C. , may be taken as the unit.

The definition of unit heat quantity makes it evident that the measurement of heat energy depends upon the specific heat of the absorbing body, and the temperature through which it is raised, so that specific heat and temperature are the factors to be considered in heat measurement.

When a solid changes to the liquid state or a liquid to the gaseous state, heat is absorbed without change in temperature, but the heat reappears when the inverse change takes place. The heat absorbed by melting ice is 80 calories, and that absorbed by boiling water is 537 calories. These numbers are termed the latent heats of fusion of ice, and of vaporization of water, for they represent the quantities of heat used up in changing 1 gram of ice at 0°C. to water, and 1 gram of water at 100°C. to steam at the same temperatures.

SUMMARY.

Carbon and hydrogen are the principal combustible bodies, and air is the important supporter of combustion. Carbon dioxide and water are formed. The rate at which heat is developed depends upon the rate at which the chemical changes take place. A rapid current of heated air, or pure oxygen, is used when a high local temperature is required. Flame is the general result of burning a combustible gas. The heat energy of combustion is the measurable equivalent of the energy of chemical attraction which existed between the

combustible body and the oxygen of the air used in its combustion. This is generally true for all chemical changes by which heat is developed. An exothermic change is when heat is developed as a result of the change; and an endothermic change is when heat is absorbed as the change takes place. In the one case energy is given out, and in the other it is absorbed by the reacting bodies. Specific heat and temperature are the two factors of heat energy.

QUESTIONS.

1. What is understood by the ignition-point of a combustible body?
2. Give a short description of two processes for the preparation of oxygen.
3. What has been omitted from the equation: $C + O_2 = CO_2$?
4. Describe and explain three characteristic experiments with oxygen gas.
5. How would you prove that a combustible body is not destroyed as it burns away?
6. Explain the term "inversion of combustion."
7. Explain how you would localize or distribute the heat to be obtained by burning a given sample of fuel.
8. Explain the terms "flame," "luminosity," and "flame structure."
9. Give a description of the Bunsen burner.
10. Give a short account of the principle of the conservation of energy.
11. Explain the terms "temperature" and "specific heat."
12. How is the specific heat of a metal determined?

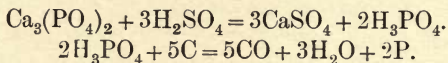
CHAPTER XIII

PHOSPHORUS AND ITS COMPOUNDS

WHEN bones are heated strongly out of contact with air, in a similar manner to coal or wood (p. 178), liquid and gaseous matters are given off, and a black residue is left in the retort. This is bone-black, and is used for various purposes. If it is completely burnt in a current of air, a white residue known as bone-ash is obtained, which consists very largely of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. This substance is used in the metallurgical operation of cupellation to absorb molten oxide of lead, and also for the extraction of phosphorus. Calcium phosphate is a constituent of the older rocks, and, when they are broken down in the slow process of soil formation, remains in the soil. It is gradually converted into a soluble form, and is then extracted by growing plants, which assimilate it, and pass it on to animals using them for food.

Extraction of Phosphorus.—Bone-ash when digested with sulphuric acid is converted into calcium sulphate and phosphoric acid. This acid is soluble in the remaining acid liquor, but the calcium sulphate is practically insoluble, and separates out in the solid state. After the acid liquid has been run off it is evaporated to a syrup in an iron vessel, mixed with charcoal powder, and further heated to a moderately high temperature. The dry mixture is then transferred to clay retorts arranged in a furnace, and there very strongly heated. Phosphorus vapour distils over, and is collected in vessels containing water. The crude phosphorus thus obtained

is purified and cast into sticks ready for use. The changes are expressed by the equations :



Natural phosphates are found in some parts of the world in considerable quantities. Apatite and phosphorite, both of which contain calcium phosphate, are the most plentiful, and may be used for the extraction of phosphorus.

Electric Smelting.—Recent improvements in the electric furnace have made it possible to smelt either a natural phosphate or bone-ash, when mixed with charcoal, for the direct production of phosphorus. The preliminary treatment with sulphuric acid is thus avoided, and a saving effected. The extremely high temperature of the furnace makes the reduction possible.

Properties of Phosphorus.—Ordinary phosphorus is an amber-yellow, waxy-looking solid, which melts at 44°C. , and boils at 290°C. It takes fire very readily, and should as a rule be handled and kept under water. It is readily dissolved by carbon bisulphide, CS_2 . When this solution is evaporated the phosphorus is left in such a finely divided condition that it bursts into flame spontaneously. It is also dissolved by a solution of caustic soda or potash ; but in this case a reaction takes place by which the gas phosphoretted hydrogen, PH_3 , is formed and liberated. This gas when impure bursts into flame directly it comes into contact with the air. It is poisonous, and has the odour of decaying fish.

When **yellow phosphorus** is heated for some time to a temperature about 240° to 250°C. out of contact with oxygen it is gradually converted into **red phosphorus**, which is a dark-red powder, insoluble in carbon bisulphide, CS_2 , and perfectly safe to handle ; but when heated in contact with air it bursts into flame. It is therefore a very different body in appearance and properties from the yellow variety, although

it is the same chemical substance. The two are *allotropic* modifications of the element.

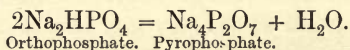
Phosphorus unites readily with metals to form phosphides, which are analogous to the sulphides in general composition; but they are not so readily obtained in the pure state. Some oxides when heated are attacked by phosphorus, and the phosphide of the metal is formed. This is the case with red-hot lime. Two important commercial materials are phosphor tin and phosphor copper, which contain phosphides of the metals. When lead is melted with an excess of phosphorus, the metal absorbs more of the non-metal than it can hold when in the solid state. This excess separates as crystals when the mass solidifies. The lead is easily dissolved by dilute nitric acid, and the phosphorus left behind as a black residue. This resembles red phosphorus closely, except in colour. It is, in fact, another allotropic modification of the element. It may be noticed here that the association of phosphorus with lead brings about a modification of the former element; and an analogy may be drawn between this change and the conversion of amorphous carbon or diamond carbon to the graphitic form by association with iron under certain conditions (p. 167).

Phosphorus is one of the common impurities in commercial iron, and passes into the metal from phosphates present in the ores, and reduced by carbon at the high temperature of the smelting furnace in which the metal is extracted.

When phosphorus burns in oxygen, or in a good supply of air, phosphoric oxide, P_2O_5 , is formed; but when the air is limited and the combustion slow, a large proportion of the product consists of lower oxides, of which phosphorous oxide, P_2O_3 , is the most important. These oxides form solutions which have a sour taste, and turn litmus red. They are, therefore, acid-forming oxides.

Phosphoric oxide is a white, powdery, volatile solid, which rapidly absorbs moisture, and deliquesces on exposure to the air. When dissolved in cold water an acid is formed, which

unites with only one proportion of a base, and forms one series of salts. It resembles nitric acid in general composition, and is known as **metaphosphoric acid**, HPO_3 . But when the solution is boiled another acid is formed, which is capable of giving three well-defined series of salts. It is tribasic (p. 153), and is known as **orthophosphoric acid**, H_3PO_4 . It is the normal or common phosphoric acid, and is readily prepared by adding red phosphorus, a little at a time, to warm concentrated nitric acid as long as the solid is taken up. The solution is then evaporated to a syrup, which is the practically pure acid. It may be dissolved in water, and used for the preparation of phosphates. The common prepared salt is disodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. When this salt is heated it loses its water of crystallization first, and then at a higher temperature parts with another molecule of water, and is converted into a salt of pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. The last change is expressed thus :



It would appear, then, that phosphoric oxide combines with water in three proportions to form three distinct acids, thus :

1. $\text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{HPO}_3$.
Metaphosphoric acid.
2. $2\text{H}_2\text{O} + \text{P}_2\text{O}_5 = \text{H}_4\text{P}_2\text{O}_7$.
Pyrophosphoric acid.
3. $3\text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4$.
Orthophosphoric acid.

They all give corresponding salts with metallic bases. The natural and prepared phosphates are for the most part ortho-salts. The salts of the other acids are not often met with in ordinary work. The phosphates of the alkaline metals and ammonium are soluble in water, and three distinct salts of each base can be obtained, if necessary. The three salts of sodium are NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 . Also, it is possible

to have two or three different bases in the same salt. Thus the well-known microcosmic salt has the formula $\text{NaNH}_4\text{HPO}_4$. It is sodium ammonium hydrogen phosphate, and forms well-defined crystals.

Phosphates of other metals are for the most part insoluble in water, but soluble in acids, and can be obtained by mixing together solutions of a soluble phosphate and of a soluble salt of the other metal. The insoluble phosphate is precipitated, and can be separated from the solution by filtration.

Phosphorous acid, H_3PO_3 , gives a series of salts called phosphites, which are not of particular importance.

Phosphorus unites directly with chlorine, bromine, and iodine, forming important compounds, which are treated fully in advanced works on chemistry.

SUMMARY.

Phosphorus is not found in the free state in Nature. Its principal natural compound is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. The element exists in at least two distinct allotropic forms. It combines readily with metals to form phosphides. Phosphor tin and phosphor copper are largely used in the preparation of alloys. The principal oxygen compounds of the element are phosphoric oxide, P_2O_5 , and phosphoric acid, H_3PO_4 . Phosphates of the common metals are easily formed.

QUESTIONS.

1. Give a short description of the usual method for obtaining phosphorus.
2. Name the common forms of phosphorus, and state how they differ from each other.
3. What happens when phosphorus burns in air?
4. Name the three acids corresponding to phosphoric oxide. To which do the common phosphates belong?
5. If you were required to obtain an insoluble phosphate of a metal, how would you proceed?

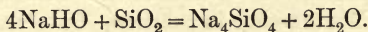
CHAPTER XIV

SILICON AND ITS COMPOUNDS WITH OXYGEN AND METALS

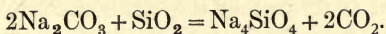
THE element silicon, although not often met with in the pure state, is present in abundance in the earth's crust, combined with oxygen and metals. Its most important compound is the dioxide, silica, SiO_2 , which in the prepared state is a perfectly white powder. One natural form of this oxide, quartz, is often found in distinct crystals, which are sometimes as transparent as glass. It is an acid-forming oxide, but as it is quite insoluble in water under ordinary conditions, this cannot be proved in the usual way. It is also very refractory in character, requiring a very high temperature to soften and fuse it.

Silica is not decomposed when strongly heated with carbon unless a metal is present into which the reduced silicon can pass as soon as it is liberated from the oxide. Thus, when a mixture of silica, charcoal, and iron is very strongly heated, silicon is reduced and passes into the metal. This is the source of silicon in commercial iron, which always contains that element, though sometimes in very small quantity. On the other hand, a specially prepared iron may contain as much as 18 per cent. of silicon. The non-metal is no doubt combined with part of the metal in the form of iron silicide, which considerably modifies the properties of the remainder of the metal with which it is associated. When iron containing silicon is dissolved in an acid, and the solution evaporated to dryness, a residue containing insoluble silica is obtained.

Silica, when finely divided, is readily dissolved by a solution of caustic soda or potash, and an alkaline salt of silicic acid is formed. With caustic soda sodium silicate, Na_4SiO_4 , is obtained :



A similar change takes place when any form of silica in a finely-divided state is fused with sodium carbonate in a platinum crucible. The reaction proceeds slowly, and carbon dioxide is liberated :



Fusion mixture, which is a mixture of sodium and potassium carbonates, is more effective than the single carbonate. The fused mass can be extracted with hot water, which dissolves out the soluble silicate together with the excess of carbonate. When dilute hydrochloric acid is added, in small quantities at a time, to this solution the excess of carbonate is decomposed without the silicic acid separating, and an excess of hydrochloric may be thus introduced. This decomposes the silicate by converting its metal into a chloride, and silica in combination with water is retained in solution.

If this acid solution is poured into a tray fitted with a bottom made of parchment paper, and floating on water in a good-sized vessel, it is found that the excess of hydrochloric acid, together with the whole of the sodium in the form of chloride, passes through the parchment into the water underneath, so that nothing but silica is left in solution in the tray. There is reason to believe that the silica is combined with water in the form of silicic acid, which will not pass through the parchment. But, although the solution can be concentrated considerably, the pure acid has not been prepared. In this respect it may be compared with the solution of carbon dioxide, which is supposed to contain carbonic acid, H_2CO_3 .

Graham, who discovered and investigated the properties of bodies taken advantage of in the above separation, gave

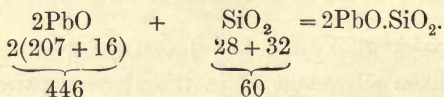
the name of **colloids** to those bodies which, when in solution, will not pass through the parchment paper, and the name of **crystalloids** to those which will so pass. He also gave the name of **dialysis** to the operation of separating crystalloids and colloids when together in solution. Substances resembling glue are colloids.

Silicic Acids.—There is evidence in favour of the possible existence of two silicic acids: orthosilicic acid, H_4SiO_4 , and metasilicic acid, H_2SiO_3 . It is readily seen that the first is tetrabasic, and is formed by the combination of silica with 2 molecules of water; the second is dibasic, and contains only 1 molecule of water.

Silicates.—The salts of silicic acid are very numerous, and are found in great variety in the earth's crust. They may be formed by the direct combination of silica with basic oxides. The facility with which a particular silicate is formed depends upon its fusibility. But if a mixture of silica and a basic oxide in the proper proportions to form a certain silicate is raised to or a little above the melting-point of the silicate, the combination will take place. In fact, in some cases the combination takes place when the mixture is exposed to a temperature below its fusing-point. This is known as **fritting** combination. In this case the two oxides must be very finely divided and intimately mixed together.

EXP. 118.—Weigh 15 grams of lead oxide, and mix with it the necessary weight of fine, hard sand (silica sand), as calculated from the equation given below. Put the mixture into a small clay crucible, and raise it to a bright-red heat in a gas muffle, or wind furnace. When thoroughly melted, pour the contents of the crucible on to an iron plate. The resulting silicate when cold is an amber-coloured glass.

The two oxides unite directly at a moderate temperature to form lead silicate:



The mode of writing the formula of a silicate adopted in the equation is the one most used, and is justified by the way in which the combination takes place.

EXP. 119.—Mix 5 grams of finely-ground red copper scale, Cu_2O , with the necessary quantity of silica sand to form the silicate $\text{Cu}_2\text{O}.\text{SiO}_2$. Heat the mixture on a clay dish in a gas muffle to a moderate red heat for half an hour. Allow the dish to cool, and grind up a little of the residue in a mortar. When examined with a lens the particles appear to be all alike. The particles of sand and cuprous oxide fit together, and the combination takes place without fusion.

FUSIBILITY OF SILICATES.

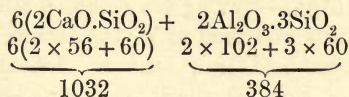
Single Silicates.—Among the common silicates those of the alkaline metals and lead have the lowest fusing-points; silicates of copper and iron take an intermediate place; while silicates of lime, magnesia, and alumina fuse only at high temperatures. But, as no silicate will resist the excessive temperature of an electric furnace, they may be described generally as fusible compounds with a wide range of fusing-points.

A normal silicate when in the fused state will, as a rule, dissolve more of its basic oxide, or of silica, whichever is presented to it. In the first case the normal silicate becomes a basic salt, and in the second an anhydro-acid salt (p. 154). The addition may either raise or lower the fusing-point of the mass. There is no general rule with regard to this change.

Complex Silicates.—It may be stated generally that if two chemical compounds, having well-defined melting-points, are mixed together in certain proportions, the resulting mixture will have a lower melting-point than either of the constituents taken singly. Silicates form the best illustration of this general principle, and every advantage is taken of it in metallurgical operations. For example, the normal silicates of lime and alumina are separately infusible at ordinary furnace temperatures; but if they are melted together, or

if arrangements are made for their simultaneous formation in certain proportions, a readily fusible double silicate is the result.

The formula for orthosilicic acid is H_4SiO_4 , or $2\text{H}_2\text{O}.\text{SiO}_2$; it is, therefore, tetrabasic. So that the normal salt of lime is $2\text{CaO}.\text{SiO}_2$, and that of alumina $2\text{Al}_2\text{O}_3.3\text{SiO}_2$. Now, either of these compounds is practically infusible at ordinary furnace temperatures, but if they are heated together in certain proportions a moderately fusible double silicate is obtained. This may be expressed by the following formula, which is usually aimed at when the double silicate is to be formed in a metallurgical operation :



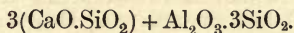
The proportions given are easily verified, and the percentage of each constituent can be calculated. If this is done, mixtures of the oxides are readily made in convenient quantities to give approximately the above composition.

EXP. 120.—1. Mix together 7 grams of quick-lime, and 3·8 grams of fine sand ; put the mixture into a carbon crucible, and heat it strongly in a wind furnace for twenty minutes. Put a lid on the pot, and place it well down in the fire, so as to expose it to the highest temperature the furnace will give. Remove the pot from the fire at the end of stipulated time, and allow it to cool. 2. Mix together 2·1 grams of alumina and 1·9 grams of fine sand, and follow the instructions given for No. 1. On examination the mixtures are found to be fitted together, and the one containing the lime may show signs of incipient fusion. 3. Grind the two mixtures thoroughly together in an iron mortar ; transfer the new mixture so obtained to the carbon crucible, and heat it again for twenty minutes under the same conditions as before. Remove the crucible from the furnace, allow it to cool, and examine the result of the experiment.

If the experiment is carefully conducted, a button of the perfectly fused double silicate will be obtained. It is very brittle and readily fractured. Very often it breaks up while cooling, which is due to unequal contraction in different parts

of the mass. The appearance of the fractured surface depends somewhat upon the furnace conditions and on the rate of cooling. It may vary from a bright glassy to a dull earthy appearance.

A similar experiment may be made with the corresponding compounds of metasilicic acid, $\text{H}_2\text{O}.\text{SiO}_2$. The composition of the most fusible double silicate of lime and alumina is given by the formula :



The metasilicate of lime will show more signs of fusion than the corresponding orthosilicate; and, if the temperature is very high, the metasilicate of alumina will soften considerably. It is, therefore, more fusible than the corresponding orthosilicate. The double silicate is also more fusible, and forms the normal slag of furnaces working at a moderate temperature. Orthosilicate slags come from hotter furnaces.

If a small quantity of a basic oxide is added to a fused silicate, it is dissolved, and exerts an influence upon (1) the fusibility of the silicate and (2) its appearance. In most cases the fusibility is increased, but this is not always so; an addition of zinc oxide, ZnO , for example, decreases the fusibility. Various colours are imparted to silicates by the addition of oxides of iron (green), copper (red), cobalt (blue), etc. Oxide of tin renders the silicate opaque, as in white enamels.

Fireclay is an acid silicate of alumina containing combined water, which, together with the fineness of its particles, renders the clay plastic when mixed with water. Its composition may be represented by $x\text{SiO}_2.2\text{Al}_2\text{O}_3.3\text{SiO}_2.2\text{H}_2\text{O}$, when $x\text{SiO}_2$ represents a variable proportion of the acid oxide. This material, when approximately pure, is very refractory; but the addition of small quantities of basic oxides increases its fusibility and renders it unfit for fire-resisting purposes. This effect depends upon the nature and proportion of the added oxide. Soda, potash, and oxide of lead exert the

greatest influence ; lime and oxide of iron are also very hurtful, the latter especially so if carbon or reducing gases are present to reduce the ferric oxide, Fe_2O_3 , to ferrous oxide, FeO . These oxides unite with the excess of silica, and fusible double silicates are formed, and if present as impurities in the clay, are injurious to its refractory character.

EXP. 121.—Mix a few grams of finely-powdered fireclay with 5 per cent. of dry sodium carbonate, which will carry about 3 per cent. of soda, Na_2O , into the mixture. Heat the mixture strongly in a carbon crucible for twenty minutes, and examine the result.

Glass.—If the experiments described above are carried out, the tendency of fused silicates to form the transparent amorphous body known as glass is clearly demonstrated. Long experience has taught the glass-maker the mixtures of silicates which give the best results for particular purposes. Thus, **window** glass is a double silicate of lime and soda ; **Bohemian** glass, which is a double silicate of lime and potash, will withstand a moderately high temperature without softening, and changes in temperature without cracking: it is, therefore, very useful for combustion-tube and for chemical apparatus generally. **Flint** glass is a double silicate of lime and lead oxide, and softens readily in an ordinary gas flame ; it is used for making glass tube which is required to be easily bent. Glass has to be carefully annealed by allowing it to cool very slowly after it has been blown into shape. The plastic state of hot glass, which extends through a wide range of temperature, renders it possible for the glass-blower to do with his material what the potter does with plastic clay. The introduction of small quantities of metallic oxides brings about the variations in colour observed in ornamental glasses ; and a very small quantity of free metal in an extremely finely divided state may influence the colour, as is the case with gold in ruby glass. The opalescence in some varieties of glass is caused by the added oxides not completely dissolving in the molten mass, and the very fine solid particles being suspended in the fluid matter while it sets.

Nomenclature of Silicates.—A system of naming, which has been very largely adopted by metallurgists, depends upon the proportion between the number of atoms of oxygen in the acid and basic portions of the given silicate. This is clearly dependent upon the assumption that a silicate is a combination of two or more oxides, one of them always being silica. Take, for example, the sodium salt of orthosilicic acid, $2\text{Na}_2\text{O}.\text{SiO}_2$. The relation here is 1 : 1, for there are 2 atoms of oxygen in each part of the compound. But with the sodium metasilicate, $\text{Na}_2\text{O}.\text{SiO}_2$, the relation is 2 : 1, for there are 2 atoms of oxygen in the acid portion to 1 atom in the basic portion. The number of atoms of the metal, which varies with its valency, does not influence the character of the silicate. The ratio 1 : 1 gives rise to **monosilicates**, and the ratio 2 : 1 **bisilicates**. But this does not account for the anhydro-acid silicates, of which there are numerous examples. Thus in the **trisilicates** the ratio is 3 : 1, and in the **sesquisilicates** it is 3 : 2. There are also silicates which contain an excess of the basic oxide, and the most important of these are included in the **subsilicates** in which the ratio is 1 : 2.

TABLE OF SILICATES.

| RATIO OF NUMBER OF ATOMS OF OXYGEN IN ACID OXIDE TO NUMBER OF ATOMS OF OXYGEN IN BASIC OXIDE. | | MONOVALENT METAL, $\text{M}'_2\text{O}$. | DIVALENT METAL, $\text{M}''\text{O}$. | TRIVALENT METAL, $\text{M}'''\text{O}_3$. |
|---|--------|---|--|--|
| 1 : 2 | Sub | $4\text{Na}_2\text{O}.\text{SiO}_2$ | $4\text{CaO}.\text{SiO}_2$ | $4\text{Al}_2\text{O}_3.3\text{SiO}_2$ |
| 1 : 1 | Mono | $2\text{Na}_2\text{O}.\text{SiO}_2$ | $2\text{CaO}.\text{SiO}_2$ | $2\text{Al}_2\text{O}_3.3\text{SiO}_2$ |
| 2 : 1 | Bi | $\text{Na}_2\text{O}.\text{SiO}_2$ | $\text{CaO}.\text{SiO}_2$ | $\text{Al}_2\text{O}_3.3\text{SiO}_2$ |
| 3 : 1 | Tri | $2\text{Na}_2\text{O}.\text{SiO}_2$ | $2\text{CaO}.3\text{SiO}_2$ | $2\text{Al}_2\text{O}_3.9\text{SiO}_2$ |
| 3 : 2 | Sesqui | $4\text{Na}_2\text{O}.3\text{SiO}_2$ | $4\text{CaO}.3\text{SiO}_2$ | $4\text{Al}_2\text{O}_3.9\text{SiO}_2$ |

The metals commonly present in silicates are: (1) Monovalent, general formula of oxide $\text{M}'_2\text{O}$, where M represents an atom of the metal; (2) divalent, $\text{M}''\text{O}$; and (3) trivalent,

M'''_2O_3 . Often all three of these types of oxides are present in the same well-defined silicate. It is the readiness with which acid, basic, and complex silicates seem to form that makes these bodies so numerous.

When a natural or prepared silicate is in the form of a glassy or stony-looking body, it is impossible to state for certain that it is a well-defined compound, although its composition can be accurately determined. But when it is found or obtained in well-defined crystals, this difficulty disappears, and an exact formula can be assigned to it. Such bodies often occur in the earth's crust, and may also be prepared artificially. In this respect it is to be borne in mind that slow cooling of a molten mass favours the formation of crystalline structure and the development of individual crystals.

Mono-, di-, and tri-valent metals are often associated in the same natural silicate, and empirical formulæ, as simple as possible, are commonly used in such cases. Thus the well-known mineral **felspar** is written empirically $KAlSi_3O_8$, and this tells the beginner very little, except that it is a double silicate of potassium and aluminium; but if it is noticed that the monovalent K' and trivalent Al''' give a tetravalent combination $(KAl)''''$, which is equivalent to 2 atoms of oxygen, the formula may be written $(KAl)O_2 \cdot 3SiO_2$, and the compound is seen to be a trisilicate. Also, potassium may be more or less completely replaced by sodium without altering the crystalline form. In this case the different compounds are isomorphous (p. 128). Isomorphism plays a very important part in the mineral world. Na_2O and K_2O ; CuO , MgO , MnO , and FeO ; Al_2O_3 , Fe_2O_3 , and Mn_2O_3 replace each other without altering the crystalline form of the minerals in which they occur.

These natural bodies of definite composition are the minerals which help to form the various rocks in the earth's crust. Thus, granite is made up of three well-defined minerals: felspar, mica, and quartz, and the crystals of these bodies were formed during the extremely slow cooling of the molten

rock. Granite is readily melted in an ordinary wind furnace, but does not recover its crystalline structure on cooling. The solidified mass resembles the slags formed in smelting operations.

SUMMARY.

Silica, SiO_2 , the only oxide of silicon, is the most generally occurring compound in the earth's crust. Quartz, flint, and sand are its commonest forms. In combination with metallic oxides it forms the natural and prepared silicates, which are a very numerous class of bodies. There are two silicic acids, which give rise to two well-defined series of compounds, orthosilicates and metasilicates. These normal silicates, when in the molten state, readily take up an excess of either silica or metallic oxides, and form basic and anhydro-acid silicates. Different silicates also mix together readily, and a large number of complex bodies are thus formed. As a rule, a complex silicate is more fusible than a single silicate. The element silicon unites with metals to form silicides. It is commonly found as an impurity in commercial iron.

QUESTIONS.

1. Give a short description of the physical and chemical properties of silica.
2. What is the general effect of mixing silicates together, upon the fusing-point of the mixture?
3. Describe an experiment in which a silicate is formed.
4. What is fireclay, and to what does it owe its plasticity?
5. How are silicates classified for metallurgical purposes?
6. What do you understand by the isomorphous substitution of one metallic oxide for another in a silicate?

CHAPTER XV

WEIGHTS, MEASURES, AND APPARATUS

THE Metric System of weights and measures, which is of French origin, is almost universally used for scientific purposes. It is a decimal system, and on that account is very easy to work with.

Length.—The unit of length is the **metre**, which is divided into 10 parts, or **decimetres**; into 100 parts, or **centimetres**; and into 1,000 parts, or **millimetres**. The Latin prefixes, *deci-*, *centi-*, and *milli-*, mean $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$, respectively, and denote the submultiples of the metre.

The Greek prefixes, *deka-*, *hecto-*, and *kilo-*, denote 10, 100, and 1,000, respectively, and are used for multiples of the metre. Thus, 1 kilometre = 1,000 metres.

Volume.—The common measure of volume is the **litre**. Its capacity is equal to that of a cube, 1 decimetre, or 10 centimetres on the side. The litre = 1 cubic decimetre = 1,000 cubic centimetres. Any volume less than a litre is usually expressed in cubic centimetres. Thus, $\frac{1}{2}$ litre = 500 cubic centimetres = 500 c.c., c.c. being the contraction for cubic centimetres.

Weight.—The unit of weight is derived from the metre; it is the weight of a cubic centimetre of pure water at its point of maximum density (4° C.), and is called the gramme or gram. The submultiples are the decigram, or $\frac{1}{10}$ gram; the centigram, or $\frac{1}{100}$ gram; and the milligram, or $\frac{1}{1000}$

gram. The Greek prefixes are used for the multiples. Thus, the kilogram = 1,000 grams.

ENGLISH EQUIVALENTS OF THE METRIC UNITS.

| | |
|------------|------------------------------|
| The metre | = 39·37 inches. |
| „ litre | = 1·76 pints. |
| „ gram | = 15·432 grains. |
| „ kilogram | = 2·2046 pounds avoirdupois. |

The equivalents of the multiples or submultiples are easily obtained by moving the decimal point to the right for multiples, and to the left for submultiples.

Thus, 1 kilometre = 39,370 inches.

1 centigram = 0·15342 grain.

The following will be found useful in making comparative measurements :

| | |
|---------------------|--------------------|
| 1 pound avoirdupois | = 7,000 grains. |
| 1 ounce | „ = 437·5 „ |
| 1 pound troy | = 5,760 „ |
| 1 ounce | „ = 480 „ |
| 1 pint | = 20 fluid ounces. |

1 pint of water at 15·5° C. weighs 20 ounces avoirdupois.

1 gallon of water at 15·5° C. weighs 10 pounds avoirdupois.

1 cubic foot of water at 15·5° C. weighs 62·4 pounds avoirdupois nearly.

The Balance.—The most casual observer is familiar with the ordinary beam scales used in everyday life ; and, as the more sensitive balance used for scientific purposes is exactly the same in principle, no difficulty should be experienced in using it. Accuracy in weighing is only a matter of care and experience.

The beginner should examine the balance he is using, and notice that it consists of an accurately made beam, supported by knife edges which rest on smooth horizontal plates or in

V-shaped grooves, and having two scale-pans suspended in a similar manner, one from each end. The points of suspension of the pans are at exactly the same distance from the point of suspension of the beam, and the two halves of the beam

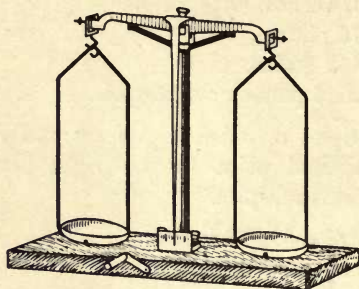


FIG. 41.

are exactly similar to each other. When the balance is properly set the pointer should be perfectly vertical if the beam is at rest, or should swing to nearly equal distances on each side of the vertical division on the scale at the foot of the supporting pillar if it is in motion. The smaller the weight required to be

added to either one side or the other in order to disturb this equality, the more sensitive the balance is, and the more accurate the weighing which can be made upon it. A cheap and sufficiently accurate form of balance is shown in Fig. 41.

The Weights.—The Metric System of weights is almost universally used for scientific purposes, and a box of gram weights containing from 100 grams to 1 milligram will be found sufficient for most purposes. The individual weights—are commonly marked as shown in the diagram.

| | | | | |
|------------|-------|-------|-------|-------|
| Grams | { 100 | 50 | 20 | 20 |
| | { 10 | 5 | 2 | 1 |
| Decigrams | 0.5 | 0.2 | 0.1 | 0.1 |
| Centigrams | 0.05 | 0.02 | 0.01 | 0.01 |
| Milligrams | 0.005 | 0.002 | 0.001 | 0.001 |

Sometimes it is found convenient to use grain weights, and sets varying from 1,000 grains to 0.5 grain would be found sufficient for the work described in this book. In converting the weight in grams given in the text into grains it will be

sufficient to multiply the weight in grams by 15.5. 1 gram = 15.432 grains.

Weighing.—The body to be weighed is usually placed in the left-hand pan, the weights in the right-hand one. The weights should be used systematically, as weighings are made more rapidly by so doing. The beam can be raised or lowered by means of a lever arrangement worked from the front of the stand, and bodies to be weighed should not be put into the pan, nor should weights be added while the beam is swinging freely. When weighing it is not necessary to wait for the beam to come to rest, for when the pointer swings to very nearly equal distances on each side of the perpendicular mark on the graduated scale in front of which it moves, the weighing is finished. Bodies which are at all likely to soil the scale-pan should be weighed in a counterpoised watch-glass or crucible. In fact, it is a good plan to make all weighings in this way, as any little inaccuracy in the balance is thus neutralized. For example, if a watch-glass is weighed, and a body then weighed in it, the difference between the two weights is the weight of the body. The beginner is strongly advised to get into the habit of writing down the results of weighings before he leaves the balance. A little practice, especially with the assistance of a teacher, will enable him to weigh accurately, and soon convince him that methodical weighing is much more rapid than an erratic putting on and pulling off of weights.

Measuring Vessels.—The volume measures of the Metric System* are almost always used in volumetric work. The cubic decimetre or litre is the most important, and contains 1,000 cubic centimetres. In the experiments described in the text the volumes used are less than a litre, and are generally expressed in cubic centimetres.

The **burette** is a long, narrow, glass tube, open at one end and fitted at the other with a tap arrangement through which

* See the table of the Metric System of weights and measures at the beginning of the chapter.

small quantities of the contained liquid can be run. The tap must be so under control that the liquid may be made to leave the burette one drop at a time, if necessary. In cheap burettes it is usual to connect the body with the nozzle by means of a piece of rubber tube, and to close this by a spring pinch-tap. A glass tap is shown in Fig. 42. A very simple and effective substitute for the pinch-tap may be made by introducing a piece of glass rod $\frac{1}{4}$ inch long, rounded at the ends, and of such diameter as to require gently forcing into the rubber tube connection between the nozzle and the body

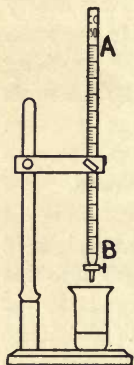


FIG. 42.

of the burette. This completely closes the burette while at rest, but when the rubber tube just over the rod is squeezed between the finger and thumb a channel in the rubber is made down the side of the rod by which the liquid can escape. On removing the pressure the burette is at once closed. The body of the burette is graduated between A and B into fifty divisions, each equal to 1 cubic centimetre, so that if a liquid is level with the zero mark at A, and is run out until it is level with B, exactly 50 cubic centimetres are delivered. If the level is reduced to some point between A and B, then the graduation mark at that point gives the volume delivered. The surface of the liquid in the burette is curved, and the readings are best made by reference to the lower or convex surface of the liquid. The burettes usually sold are not very accurate; but if any connected set of measurements are made with the same burette a slight inaccuracy does not appreciably affect the results. For liquids which corrode rubber tube, burettes with glass taps must be used.

Measuring Flasks are usually sold in four sizes—*i.e.*, 1,000 c.c., 500 c.c., 250 c.c., and 100 c.c. They sometimes have two graduation marks on the neck, one to contain and

one to deliver. As these flasks expand or contract as they are heated or cooled, the reading is only strictly true at the temperature at which the graduation was made. This is usually the normal temperature of a laboratory, *i.e.*, 15° C. Thus, if a liquid is poured into the dry flask until the level reaches the lower graduation mark *b*, Fig. 43, the flask contains the registered volume of liquid; but if the level

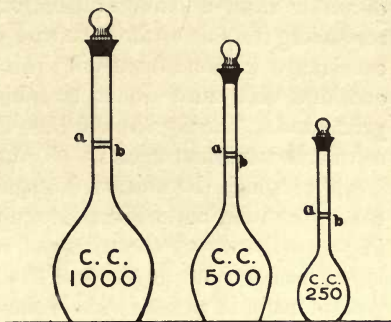


FIG. 43.

is brought to the upper graduation mark *a*, then it will deliver the registered quantity if the liquid is poured into another vessel. The extra liquid between the two marks compensates for that which adheres to the sides of the flask after the main bulk has been poured out.

Three very useful measures are shown in Fig. 44, which may be used for rough measurements. They deliver 500, 250, and

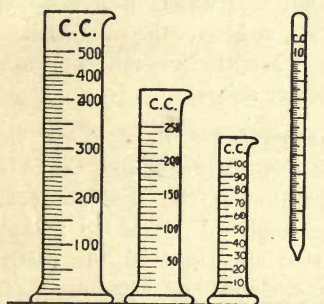


FIG. 44.

50 c.c. respectively. For the rapid measurement of a few cubic centimetres of liquid a pipette can be made by drawing off to a point in the gas flame a piece of glass tube about $\frac{3}{16}$ of an inch internal diameter and 8 inches long. To graduate it into cubic centimetres, dip the narrow end into water, and when some of the liquid has

entered, remove the tube and let out as much of the liquid as will run from the narrow end. Without disturbing

the small quantity of liquid not delivered, close the narrow end with a little stiff grease, and run in at the open end 1 c.c. of water from a burette; mark the level of the liquid by scratching the side of the tube with a file; run in a second cubic centimetre without disturbing the first, and mark as before; continue this until about two-thirds of the tube has been graduated. The pipette will then deliver the number of cubic centimetres marked upon it. To use it, place the tube in the liquid of which the measured quantity is required; the liquid enters the tube, and when the required quantity is in, place the finger on the top of the tube and remove it. To deliver the liquid, remove the finger, and it will run out. A very useful pipette made in various sizes is shown in Fig. 44.

Wash-bottle.—A very convenient form of wash-bottle for quantitative work is shown in Fig. 45. It consists of a glass

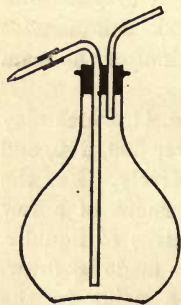


FIG. 45.

flask, A, fitted up as shown in the figure. The nozzle, B, is attached by means of a piece of rubber tube, and the neck, C, is bound with a layer of thick string. The flexible nozzle allows of a stream of water being sent in any required direction. If the flask is thin the water in it may be raised to boiling, either on the sand-bath or on wire gauze, when the necessity of washing with hot water arises.

Other Apparatus.—In devising the experiments described in the text, the chief aim has been to use such apparatus as the student in an elementary laboratory may be expected either to possess or to have access to. Expensive apparatus of the easily-broken type has been either excluded or attempts have been made to imitate it in a simple manner. When more accurate apparatus than that described can be used, better results may be expected. But the student often gains some knowledge by fitting up a piece of apparatus consisting

of several parts, which by the ingenuity of the glass-blower may be obtained complete. The principle involved in the saying, "You press the button, we do the rest," is no doubt useful for many purposes, but it is bad from an educational point of view.

The table furnace shown in Fig. 8 was evolved from a simpler form consisting of an iron stand carrying some loose fireclay slabs, and having two ordinary Bunsen burners underneath. In the first modification the movable burners were replaced by three fixed burners, and in the last the fireclay slabs were replaced by a rectangular fireclay chamber, surmounted by a sheet-iron tube to increase the draught. The temperature obtained in this chamber is very high for a table furnace, and experiments which in the ordinary form of furnace either fail or are only partially successful can be carried out with it.

Conical flasks are much more convenient for general work than the ordinary globular variety. The 8, 12, and 16 ounce sizes are the most useful.

Porcelain Crucibles. — The best Berlin crucibles are the cheapest in the end, and Nos. 1 and 2 are the useful sizes.

Combustion-tube, with walls of medium thickness, should be selected. Experiments are often a failure in thick-walled tubes, because the heat from the ordinary Bunsen flame is not able to penetrate sufficiently. On the other hand, a thin-walled tube is liable to blow out when hot, if the gas pressure inside is greater than that of the atmosphere outside.

Clay roasting-dishes are very handy for muffle work, and Morgan's No. 1 is a useful size.

APPENDIX

TABLE OF ELEMENTS, WITH SYMBOLS AND ATOMIC WEIGHTS

NON-METALS.

| NAME. | SYMBOL. | ATOMIC WEIGHT. | NAME. | SYMBOL. | ATOMIC WEIGHT. |
|--------------|---------|----------------|----------------|---------|----------------|
| Argon ... | A | 40·0 | Iodine ... | I | 126·54 |
| Arsenic ... | As | 74·9 | Nitrogen ... | N | 14·01 |
| Bromine ... | Br | 79·76 | Oxygen ... | O | 15·96 |
| Boron ... | B | 10·9 | Phosphorus ... | P | 30·96 |
| Carbon ... | C | 11·97 | Silicon ... | Si | 28·0 |
| Chlorine ... | Cl | 35·37 | Selenion ... | Se | 78·87 |
| Fluorine ... | F | 19·06 | Sulphur ... | S | 31·98 |
| Hydrogen ... | H | 1·0 | Tellurion ... | Te | 127·7 |

COMMON METALS.

| | | | | | |
|---------------|----|--------|----------------|----|--------|
| Aluminium ... | Al | 27·04 | Magnesium ... | Mg | 23·94 |
| Antimony ... | Sb | 119·6 | Manganese ... | Mn | 54·8 |
| Barium ... | Ba | 136·86 | Mercury ... | Hg | 199·8 |
| Bismuth ... | Bi | 207·5 | Molybdenum ... | Mo | 95·9 |
| Cadmium ... | Cd | 111·7 | Nickel ... | Ni | 58·6 |
| Calcium ... | Ca | 39·91 | Platinum ... | Pt | 194·3 |
| Chromium ... | Cr | 52·45 | Potassium ... | K | 39·03 |
| Cobalt ... | Co | 58·6 | Silver ... | Ag | 107·66 |
| Copper ... | Cu | 63·18 | Sodium ... | Na | 22·995 |
| Gold ... | Au | 196·7 | Strontium ... | Sr | 87·3 |
| Iron ... | Fe | 55·88 | Tin ... | Sn | 117·35 |
| Lead ... | Pb | 206·92 | Zinc ... | Zn | 64·88 |

REMARKS.—Sb from stibium ; Hg from hydrargyrum ; K from kalium ; Cu from cuprum ; Ag from argentum ; Au from aurum ; Na from natrium ; Fe from ferrum ; Sn from stannum ; Pb from plumbum. The names of the more important elements are printed in thick type.

RARE METALS.

| NAME. | SYMBOL. | ATOMIC WEIGHT. | NAME. | SYMBOL. | ATOMIC WEIGHT. |
|----------------------|---------|----------------|----------------------|---------|----------------|
| Beryllium ... | Be | 9·08 | Ruthenium ... | Ru | 103·5 |
| Cæsium | Cs | 132·7 | Samarium ... | Sm | 150·0 |
| Cerium ... | Ce | 142·2 | Scandium ... | Sc | 43·97 |
| Didymium ... | D | 145·0 | Tantalum ... | Ta | 182·0 |
| Erbium ... | E | 166·0 | Terbium ... | Tr | 160 0 |
| Gallium ... | Ga | 69·9 | Thallium ... | Tl | 203·7 |
| Germanium ... | Ge | 72·32 | Thorium ... | Th | 231·96 |
| Indium ... | In | 113·4 | Thulium ... | Tu | 169·4 |
| Iridium ... | Ir | 192·5 | Titanium ... | Ti | 48 |
| Lanthanum ... | La | 138·5 | Tungsten ... | W | 183·6 |
| Lithium .. | Li | 7·01 | Uranium ... | U | 239·8 |
| Niobium ... | Nb | 93·7 | Vanadium ... | V | 51·1 |
| Osmium ... | Os | 191·0 | Ytterbium ... | Yb | 172·6 |
| Palladium ... | Pd | 106·2 | Yttrium .. | Y | 89·9 |
| Rhodium ... | Rh | 103·1 | Zirconium ... | Zr | 90·4 |
| Rubidium ... | Rb | 85·2 | | | |

CORRECTION OF THE VOLUME OF A GAS FOR TEMPERATURE, PRESSURE, AND WATER VAPOUR.

Correction for Temperature.—Gases expand $\frac{1}{273}$ of their volume for every increase of 1° C. in their temperature and contract in the same degree when their temperature is decreased (law of Charles). Now, suppose the gas to be corrected were cooled to 0° C., its volume divided into 273 parts, and the whole again raised a degree at a time to the original temperature. Then for a rise of 1° the increased volume would be represented by 274, for 5° by 278, for t° by $273+t$. Therefore the ratio between the volume of a gas at t° C. and its volume at 0° C. is expressed by $(273+t) : 273$, and the volume at 0° C. is found by multiplying the volume at t° C. by $\frac{273}{273+t}$. If the temperature of the gas is below 0° C. t is negative, and it is to be subtracted from, and not added to, 273.

Correction for Pressure.—The volume of a gas is inversely as the pressure it sustains, or the volume decreases in the same proportion as the pressure increases, and *vice versa* (law of Boyle and Marriott). The pressure to which a gas is subjected when standing over a liquid with the liquid at the same level inside and outside the containing vessel, is exactly that of the air outside, and can be determined in millimetres of mercury by reading the barometer. If the normal pressure be taken as equal to 760 millimetres of mercury, and the pressure of the gas to be corrected is equal to p millimetres, then the ratio between the volumes at p and at 760 is $\frac{760}{p}$, and the corrected volume is found by multiplying the volume at p by $\frac{p}{760}$. p may be greater or less than 760.

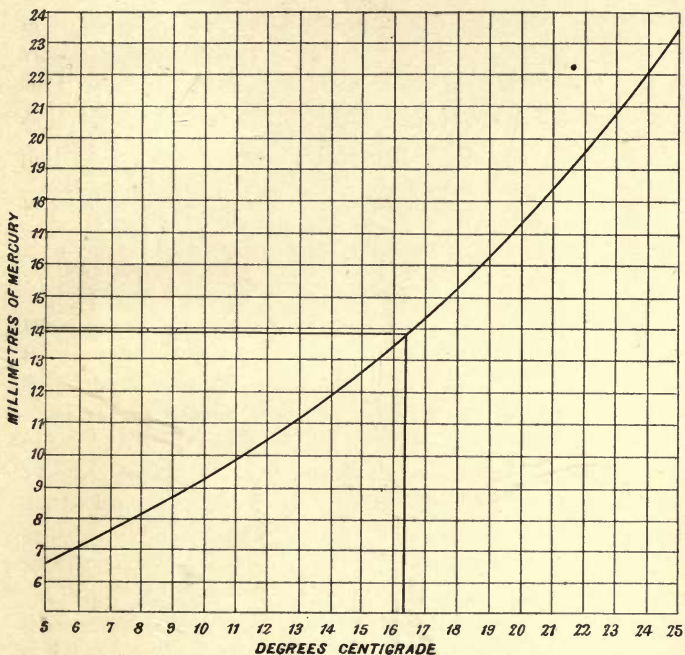
Correction for Water Vapour.—A gas standing over water becomes saturated with the vapour of the liquid, but the weight of the volume of water vapour present depends upon the temperature of the gas. Thus, at a given temperature a definite weight of water gas will mix with the other gas, and, by Dalton's law of partial pressures, will exert its own share of the total pressure of the moist gas. But when two gases are mixed together their partial pressures are proportional to their original volumes. Therefore, if the partial pressure of water vapour at the temperature of the moist gas is known, the volume of the water vapour can be calculated. A diagram showing the pressure of saturated water vapour for a limited range of temperature is given on next page.

The temperature of the gas is to be taken in degrees Centigrade, and the tension of the vapour at that temperature is expressed in millimetres of mercury.

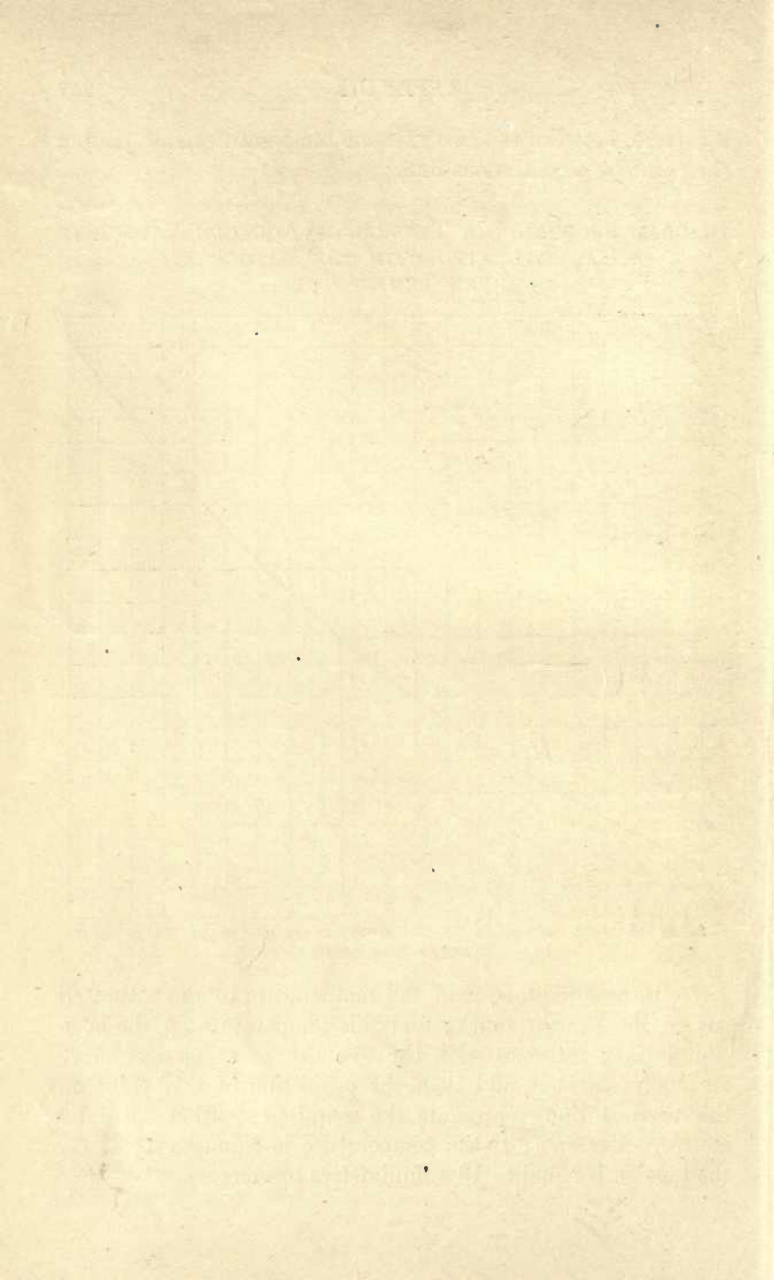
The temperature is measured on the horizontal lines, and the tension on the vertical ones. The curve is obtained by marking off on the diagram the results of a number of experiments for determining the vapour tension at varying tem-

peratures, between the two extreme temperatures, and joining the point by a continuous line.

DIAGRAM SHOWING THE TENSION OF AQUEOUS VAPOUR IN A GAS SATURATED WITH THE VAPOUR AT A GIVEN TEMPERATURE.



To use the diagram, read the temperature of the saturated gas to the nearest tenth; find this temperature on the horizontal line; estimate with the eye the point on the curve vertically above it, and then the projection of this point on the vertical line represents the required tension in millimetres. Example: If the temperature is equal to 16.3° C., the tension is equal to 13.8 millimetres of mercury.



INDEX

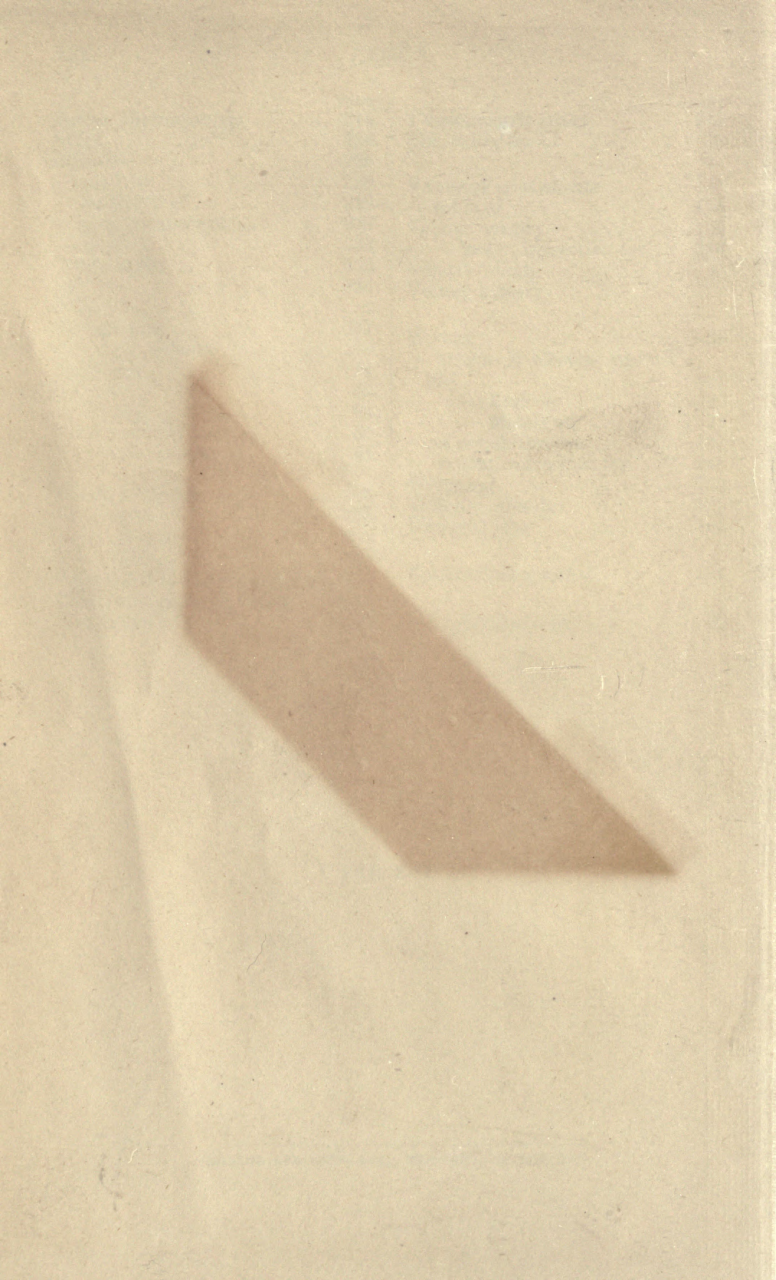
| | PAGE | | PAGE |
|--------------------------------|---------|-------------------------------|------------|
| ACID, hydrochloric | 69 | Boyle and Marriott, law of .. | 246 |
| — nitric | 78 | Brin's process | 202 |
| — sulphuric | 63 | Bromine | 76 |
| Acid-forming oxides | 137 | Bunsen cell | 112 |
| Acids, action of, on alloys .. | 106 | Burette | 240 |
| — — — — iron | 105 | | |
| — basicity of | 153 | CALORIE | 219 |
| — constitution of | 152 | Carbide of iron | 105 |
| — phosphoric | 224 | Carbon | 163 |
| — silicic | 228 | — dioxide | 172 |
| Action, electro-chemical .. | 107 | — monoxide | 174 |
| Air gas, composition of .. | 180 | — reduction by | 185 |
| Alkalies, fixed | 83 | Carbonates and acids .. | 171 |
| — volatile | 83 | — natural | 167 |
| Allotropic modification .. | 57, 166 | — prepared | 168 |
| Alloys, action of acids on .. | 106 | Carbonic oxide, reduction by | 190 |
| Aluminium | 90 | Cast iron | 105 |
| Amalgamated zinc | 108 | Cell, Bunsen | 112 |
| Ammonia | 82 | Change, chemical | 4 |
| Ammonium chloride | 81 | — endothermic | 177, 214 |
| Analysis | 67 | — exothermic | 177, 214 |
| Anhydride | 138 | — physical | 3 |
| Apatite | 222 | Charcoal | 164 |
| Atom, definition of | 42 | — combustion of | 165 |
| Atomic heat | 128 | Charles, law of | 245 |
| — weights | 125 | Chemical change | 4 |
| Atomicity | 131 | — combination, laws of .. | 47, 52 |
| Atoms and molecules, theory | | — equation | 49, 54, 67 |
| of | 51 | — equivalents | 116 |
| Avogadro, law of | 43 | — — table of | 125 |
| | | Chlorate of potassium .. | 75 |
| BALANCE | 237 | Chloride of ammonium .. | 81 |
| Basic oxides | 136 | Coal | 177 |
| Basicity of acids | 153 | — gas | 179 |
| Battery, voltaic | 112 | Colloids | 228 |
| Black oxide of manganese .. | 72 | Colouring of massicot .. | 10 |
| Bone ash | 221 | Combustion | 200 |

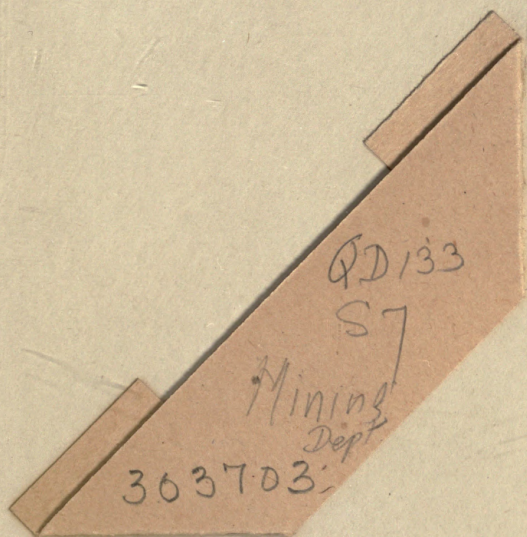
| | PAGE | | PAGE |
|------------------------------|-------------|------------------------------|----------|
| Combustion, explosive .. | 206 | FELSPAR | 234 |
| — inversion of .. | 207 | Fixed alkalies .. | 83 |
| — of charcoal .. | 165 | Flame | 208 |
| Common salt .. | 37, 69 | — luminosity of .. | 210 |
| Complex oxides .. | 137 | — structure of .. | 209 |
| — silicates .. | 229 | Flasks, conical .. | 243 |
| Composition, percentage .. | 65 | Fritting | 228 |
| Compound, definition of .. | 41, 47 | Fusibility of silicates .. | 229 |
| Conical flasks .. | 243 | | |
| Conservation of energy .. | 211, 212 | GAS, coal | 179 |
| — — matter .. | 35 | Gases | 3 |
| Constitution of acids .. | 152 | — diffusion of .. | 31 |
| Copper, oxidation of .. | 10 | Glass | 232 |
| Crystallization, water of .. | 147 | Gold, subdivision of .. | 36 |
| Crystalloids .. | 228 | Graham | 227 |
| Crystals .. | 149 | Graphite | 163 |
| Crucibles, porcelain .. | 243 | | |
| Current, electric .. | 109 | HEAT, action of, on salts .. | 157 |
| Cyanide, reduction by .. | 195 | — — — water .. | 30 |
| | | — atomic | 128 |
| DENSITY | 33 | — definition of .. | 211 |
| — of vapour .. | 126 | — measurement of .. | 214 |
| Dialysis .. | 228 | — reduction by .. | 182 |
| Diffusion of gases .. | 31 | — specific | 217 |
| Dioxide, carbon .. | 172 | Hydrochloric acid .. | 69 |
| — sulphur .. | 94 | — — and metals .. | 86-91 |
| Dissociation .. | 82, 91, 101 | Hydrogen, preparation of .. | 24, 94 |
| Divisibility of matter .. | 36 | — properties of .. | 25 |
| Double salts .. | 155 | — reduction by .. | 188 |
| Drossing .. | 9 | | |
| | | IGNITION point .. | 201 |
| ELECTRIC current .. | 109 | Indicator, methyl-orange .. | 141 |
| — — action of, on water .. | 27 | — litmus | 136 |
| Electricity, reduction by .. | 184 | Inversion of combustion .. | 207 |
| Electro-chemical action .. | 107 | Iodine | 76 |
| Electrolysis .. | 111 | Ions | 111 |
| Electrolyte .. | 111 | Iron | 24 |
| Element, definition of .. | 41 | — action of acids on .. | 105 |
| Elements, valency of .. | 131 | — carbide | 105 |
| Endothermic change .. | 177, 214 | — cast | 105 |
| Energy .. | 4 | — oxidation of .. | 12 |
| — conservation of .. | 211, 212 | — pyrites | 61 |
| — kinetic .. | 211 | — rusting of .. | 15 |
| — potential .. | 212 | — wrought | 105 |
| Equation, chemical .. | 49, 54, 67 | Isomorphism .. | 128, 156 |
| — thermo-chemical .. | 201 | | |
| Equivalents, chemical .. | 116 | KINETIC energy .. | 211 |
| — — table of .. | 125 | | |
| Exothermic change .. | 177, 214 | LAW of Avogadro .. | 43 |
| Explosive combustion .. | 206 | — — Boyle and Marriott .. | 246 |
| Extraction of phosphorus .. | 221 | — — Charles .. | 245 |

| | PAGE | | PAGE |
|---|--------|-----------------------------|--------|
| Laws of chemical combina- tion | 47, 52 | Oxidation of lead | 8 |
| Lead, oxidation of | 8 | — — mercury | 17 |
| — red | 10 | — — tin | 12 |
| Levigation | 9 | Oxide, nitric | 100 |
| Litmus indicator | 136 | — nitrous | 99 |
| Liquids | 2 | Oxides, acid-forming .. | 137 |
| Luminosity of flame .. | 210 | — basic | 136 |
| MAGNESIUM | 23 | — complex | 137 |
| Malleability | 8 | — nomenclature of .. | 138 |
| Manganese, black oxide of .. | 72 | — table of | 160 |
| Mass | 33 | Oxygen | 20 |
| Massicot, colouring of .. | 10 | — preparation of | 202 |
| Matter, conservation of .. | 35 | — properties of | 204 |
| — definition of | 33 | PEROXIDE, nitric | 100 |
| — divisibility of | 36 | Phosphoric acid | 224 |
| — physical states of .. | 2 | Phosphorus | 222 |
| Measurement of heat | 214 | — extraction of | 221 |
| — — temperature | 215 | — red | 222 |
| Mechanical mixtures | 50 | — yellow | 222 |
| Mercury, oxidation of | 17 | Physical change | 3 |
| — red oxide of | 38 | — states of matter .. | 2 |
| Metals, action of, on water .. | 22 | Preparation of oxygen .. | 202 |
| — and hydrochloric acid .. | 86, 91 | Prepared carbonates .. | 168 |
| — — nitric acid | 96 | Porcelain crucibles .. | 243 |
| — — sulphuric acid | 91 | Potassium chlorate .. | 75 |
| — reduction by | 193 | Potential energy | 212 |
| Methyl-orange | 83 | Properties of oxygen .. | 204 |
| — orange indicator | 141 | Pyrites, iron | 61 |
| Metric System | 236 | REACTION, reduction by .. | 196 |
| Mixtures, mechanical | 50 | Red lead | 10 |
| Molecule, definition of .. | 42 | — phosphorus | 222 |
| Molecules and atoms, theory of | 51 | — oxide of mercury .. | 38 |
| Monoxide, carbon | 174 | Reduction by carbon .. | 185 |
| NATURAL carbonates | 167 | — — carbonic oxide .. | 190 |
| Nitric acid | 78 | — — cyanide | 195 |
| — — and metals | 96 | — — electricity | 184 |
| — oxide | 100 | — — heat | 182 |
| — peroxide | 100 | — — hydrogen | 188 |
| Nitrogen | 20 | — — metals | 193 |
| Nitrous oxide | 99 | — — reaction | 196 |
| Nomenclature of oxides .. | 138 | Roasting | 61 |
| — — salts | 151 | Rusting of iron | 15 |
| — — silicates | 233 | SALT, common | 37, 69 |
| OXIDATION | 19 | Saltpetre | 78 |
| — of copper | 10 | Salts, action of heat on .. | 157 |
| — — iron | 12 | — double | 155 |
| | | — nomenclature of .. | 151 |
| | | — table of | 160 |

| | PAGE | | PAGE |
|-----------------------------------|------|---------------------------------|------|
| Scales, thermometric | 216 | Thermometric scales | 216 |
| Silica | 226 | Tin, oxidation of | 12 |
| Silicates | 228 | | |
| — complex | 229 | VALENCY of elements | 131 |
| — fusibility of | 229 | — table of | 133 |
| — nomenclature of | 233 | Vapour density | 126 |
| — table of | 233 | — — water, correction for | 246 |
| Silicic acids | 228 | Volatile alkali | 83 |
| Silicon | 226 | Voltaic battery | 112 |
| Solids | 2 | | |
| Specific heat | 217 | WATER | 21 |
| Structure of flame | 209 | — action of electric current | |
| Sulphides | 61 | on | 27 |
| Sulphur | 55 | — — — heat on | 30 |
| — dioxide | 94 | — — — metals on | 22 |
| Sulphuric acid | 63 | — of crystallization | 147 |
| — — and metals | 91 | — vapour, correction for | 246 |
| | | Weighing | 239 |
| TABLE of oxides | 160 | Weights, atomic | 125 |
| — — salts | 160 | Wrought iron | 105 |
| — — silicates | 233 | | |
| — — valency | 133 | YELLOW phosphorus | 222 |
| Temperature, measurement of | 215 | | |
| Thermo-chemical equation | 201 | ZINC, amalgamated | 108 |
| Thermometer | 215 | | |

THE END





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